Outline of Quantitative Analysis

BY

W. R. LANG

AND

ALFRED TINGLE

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Outlines of Quantitative Analysis

INCLUDING EXAMPLES OF

Analysis of Simple Minerals and Mineral Products.

BY

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16648
4/5/21

UNIVERSITY PRESS
TORONTO
1911

Part I. was written some time ago as a systematic guide for students in the laboratory of the University of Toronto and has already been published under the title *Outlines of Qualitative and Quantitative Analysis*, (W. R. Lang, University Press, 1910). The methods described are all standard ones and too well known to require specific acknowledgment of their original sources.

In Part II., while recognising that it is undesirable to overburden the text of a book of this class with references to original articles, the insertion of some seemed frequently called for and where this was so we have not hesitated to give them. The student is strongly advised to consult these references and to follow on from them to others, as his outlook on Analytical Chemistry will be greatly broadened by so doing.

We wish to acknowledge our indebtedness to W. F. Hillebrand's *Analysis of Silicates and Carbonate Rocks* (*U.S. Geological Survey, Bull. No. 303*). For the analysis of Coal, the procedure given is similar to that recommended in the *Report of the American Chemical Society's Committee on Coal Analysis*, (*Journal, vol. XX.*). Our thanks are also due to Professor W. A. Noyes for his kindness in privately calling our attention to the merits of the gravimetric method for determining Manganese in Spiegel, described in ***183.***

The electrolytic methods given in the text do not include any which call for the use of mercury cathodes, rotating electrodes or more recent elaborations: descriptions of these will be found in the journals or in such text books as Edgar F. Smith's *Electro Analysis*. To the latter we would also refer the student for information on such matters as sources of current, construction of rheostats and the choice of electrical measuring instruments.

The authors will be grateful if defects or mistakes are brought to their notice.

TORONTO,
MARCH, 1911.

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PART I.

OUTLINES OF QUANTITATIVE ANALYSIS.

QUANTITATIVE ANALYSIS.

The instructions contained in the author's *Outline of Qualitative Analysis* are intended to familiarise the student with the appearance and properties of substances and by means of this knowledge to determine of what a substance is composed, *i.e.*, what metal or metals are contained in it and what acid radicle or radicles. In the following pages is given a short and concise account of how the *amounts* of these bodies are estimated, in other words, an introduction to quantitative anlysis. It can not be too strongly impressed on the student at this stage the absolute necessity of orderly and methodical work, complete precipitation, complete washing of precipitates and all-round cleanliness in manipulation; the loss of one drop of a solution adhering to a beaker may occasion an error of several per cent. The student should also enter in his note book the details of each operation as it is done and not wait to "write it up" afterwards. The laboratory note-book must be kept in such a way that reference to previous work can readily be made.

1. There are two great principles on which the quantitative determination of substances is based, GRAVIMETRIC and VOLUMETRIC. In gravimetric analysis the element to be estimated is converted into a stable and, in most cases, insoluble compound, usually by precipitation under proper conditions with some reagent or reagents, and this precipitate *of known composition* accurately weighed. From this is calculated the amount of the substance under examination. For example, the amount of silver in an alloy is wanted: a weighed portion of the alloy is therefore dissolved in nitric acid and the silver precipitated by hydrochloric acid as chloride (***AgCl***). This precipitate is washed, dried, fused in a porcelain crucible and weighed; from this weight is calculated the amount of silver present. Conversely, chlorine is estimated by precipitation with silver nitrate. In like manner—

To estimate	Barium,	convert it into	$BaSO_4$,	ignite this precipitate and weigh as	$BaSO_4$.
" "	Sulphur,	" "	$BaSO_4$,	" " " " "	$BaSO_4$.
" "	Aluminium,	" "	$Al(OH)_3$,	" " " " "	Al_2O_3.
" "	Iron,	" "	$Fe(OH)_3$,	" " " " "	Fe_2O_3.
" "	Chromium,	" "	$Cr(OH)_3$,	" " " " "	Cr_2O_3.
" "	Copper,	" "	$Cu(OH)_2$,	" " " " "	CuO.
" "	Magnesium,	" "	$MgNH_4PO_4$,	" " " " "	$Mg_2P_2O_7$.
" "	Phosphorus,	" "	$MgNH_4PO_4$,	" " " " "	$Mg_2P_2O_7$.
" "	Arsenic,	" "	$MgNH_4AsO_4$,	" " " " "	$Mg_2As_2O_7$.
" "	Calcium,	" "	CaC_2O_4,	" " " " "	CaO.
" "	Chlorine,	" "	$AgCl$	" " " " "	$AgCl$.
" "	Tin,	" "	SnS,	" " " " "	SnO_2.
" "	Nickel,	" "	$Ni(OH)_2$,	" " " " "	NiO.
" "	Lead,	" "	$PbSO_4$,	" " " " "	$PbSO_4$.
" "	Manganese,	" "	$MnCO_3$,	" " " " "	Mn_3O_4.
" "	Zinc,	" "	ZnS,	ignite in an atmosphere of hydrogen and weigh as	ZnS.
" "	Cobalt,	" "	$Co(OH)_2$,	" " " " "	Cobalt.
" "	Antimony	" "	Sb_2S_3,	ignite with nitric acid and weigh as	Sb_2O_4.
" "	Cadmium,	" "	CdS,	and weigh in this form on a tared filter.	
" "	Mercury,	" "	HgS,	" " " " " "	
" "	Potassium,	" "	$PtCl_4 2KCl$,	" " " " " "	
" "	Ammonium,	" "	$PtCl_4 2NH_4Cl$,	" " " " " "	
" "	Carbonic acid, absorb it in a weighed amount of potassium hydrate.				

2. In order to ascertain the amount of the element or acid radicle that corresponds to the compound weighed, the weight of such precipitate is multiplied by a factor (which the student should obtain for himself) whose denominator is the formula-weight of the compound and whose numerator is the number representing the weight of that element or acid radicle contained in it. For example; a barium sulphate precipitate weighed 2.5 grams, the weight of barium contained in this will be $2.5 \times \frac{137}{233}$ grams, there being 137 grams of barium contained in every 233 grams of its sulphate. [$Ba = 137$, $S = 32$, $O_4 = 64$; total $= 233$]. Likewise, if in order to estimate the amount of sulphur contained in a sample of (say) coal, 5 grams of the sample yielded, after suitable treatment, an amount of barium sulphate which, when dried, weighed .25 gram, the 5 grams of coal must have contained $.25 \times \frac{32}{233}$ gram of sulphur, *i.e.*, $\frac{.25 \times 32 \times 100}{233 \times 5}$ per cent.

3. Since the process of precipitating, washing, drying and weighing precipitates occupies considerable time, more expeditious methods are often employed, use being made of solutions of reagents of known strength, and estimations done in this way come under the head of VOLUMETRIC ANALYSIS. In the first of the two examples above, that of the determination of barium, the reaction between a soluble salt of barium and a soluble sulphate may be represented by the equation,

$$\underset{\underbrace{137+2\times35.5}_{208}}{\mathrm{BaCl_2}} + \underset{\underbrace{2\times23+32+4\times16}_{142}}{\mathrm{Na_2SO_4}} = \mathbf{BaSO_4} + 2\mathrm{NaCl}$$

every 142 grams of Na_2SO_4 will *exactly* convert 208 grams of $BaCl_2$ into $\mathbf{BaSO_4}$. If, then, a solution of sulphate of soda (calculated as the anhydrous salt) be made *of known strength* and carefully run into the solution of barium chloride till it causes no further precipitate, the volume of solution used being known and the amount of sulphate of soda contained in that volume likewise known, from this the quantity of barium chloride present in the solution experimented on is at once ascertained.

4. Such solutions of known strength are called ***Standard Solutions:*** a known weight of the reagent is dissolved in a definite volume of water and the amount of such reagent contained in each c.c. of the solution is therefore known. Suppose a solution of silver nitrate is made containing .017 gram of the salt in every c.c., this amount (.017 gram) is capable of precipitating .00355 gram of chlorine in the form of silver chloride. If 100 c.c. of a solution of common salt requires 40 c.c. of this silver solution to complete the chemical change represented by the equation $NaCl + AgNO_3 = \mathbf{AgCl} + NaNO_3$, then that volume of sodium chloride solution will contain 40 × .00355 grams chlorine, and from this the amount of common salt can be calculated. The process of running a standard solution into the one whose strength is being determined is known as *titration;* in the example given, the salt solution is said to be *titrated* with standard silver nitrate.

5. The instruments used for measuring liquids are—***Graduated Flasks, Cylinders*** or ***Test-mixers, Pipettes*** and ***Burettes.*** The first are flasks that contain a certain volume of liquid when filled up to a mark cut on the neck. These are of various sizes, from 50 c.c. to 1000 c.c. (1 litre) and the mark is usually placed at such a place that, when filled to that mark, the flask will *contain* the exact number of cubic centimetres that its nominal capacity indicates. It must be remembered that this will not be the amount that it will *deliver* if emptied, for some will necessarily adhere to the walls.

6. Graduated Cylinders, or ***Test-mixers*** as they are called, are useful for measuring large quantities of liquids.

7. The ***Pipette*** is a glass tube, usually with a cylindrical bulb in the middle, drawn to a point at its lower end, with a graduation mark indicating its capacity to *deliver* a specified volume of liquid. A pipette should be allowed to empty itself and the last few drops that collect at the narrowed end, after it is held in a perpendicular position for about 15 seconds, blown out. Before filling a pipette with a solution it should, if wet, be washed out with a little of the liquid it is intended to measure. Pipettes vary in capacity from 1 c.c. to 100 c.c.

8. Burettes are graduated almost through their entire length in tenths of a cubic centimetre and the contents are drawn off by a tap at the lower end. A burette should be washed out with the solution it is going to contain before it is finally filled for use.

9. Reading Graduated Instruments. A liquid in a tube has not a plane surface but, owing to capillarity, it has a curved one known as the *meniscus;* in selecting what part of this curve is to be observed in reading the volume of a liquid, it is customary to take the graduation on the tube that corresponds with the *lowest point of the meniscus.*

10. The methods in use in volumetric analysis are based mainly on three classes of reactions, ***Neutralisation, Oxidation or Reduction,*** and ***Precipitation.***

11. Neutralisation of an alkali with an acid and the converse. The former is known as *alkalimetry* and the latter as *acidimetry*. Here the exact amount of "standard solution" required to neutralise the other substance determines the amount of acid or alkali that the sample contains. To know when neutralisation is complete an "indicator" is employed which will give definite and different colours with acids and alkalies; thus the "end-point" of the reaction, for example, when sulphuric acid has converted all of a sample of potassium hydrate into potassium sulphate, will be shown by the indicator which was (say) red with the alkali turning (say) colourless.

12. Oxidation or Reduction. Here the amount of the substance is determined by the quantity of "standard solution" required to change it from a higher state of oxidation to a lower, or *vice-versa*.

13. Precipitation. The simplest example of this is when a "standard solution" of silver nitrate is added to a solution of a chloride giving a precipitate of silver chloride. The reaction is complete, that is, the "end-point" is reached, when the addition of another drop of the reagent causes no further precipitation of silver chloride.

14. Indirect Methods are also often employed. For example, iodine is capable of very accurate determination by "standard solutions" of sodium thiosulphate, and a number of substances can liberate iodine quantitatively from potassium iodide. The amount of such substance can therefore be *indirectly* determined by estimating the *iodine* it has set free. A still more indirect example is the case of chromate of potassium and hydrochloric acid, which under certain conditions yield free chlorine; the free chlorine when passed into a solution of potassium iodide liberates its equivalent of iodine and this last can be determined by titration with thiosulphate. Hence the amount of *chromium* is found.

15. Standard Solutions are solutions of known strength, containing a definite weight of a substance uniformly distributed throughout a definite volume of solvent. Such a solution *may* be made of any strength provided such strength is known. A solution of common salt containing 10 grams in every litre (1000 c.c.) would be a standard solution and each c.c. would contain .01 gram salt which would be capable of precipitating .0184 gram silver as chloride, for, $\underbrace{AgNO_3}_{\substack{108+14+48\\170}} + \underbrace{NaCl}_{\substack{23+35.5\\58.5}} = \mathbf{AgCl} + NaNO_3$, *i.e.*, 58.5 grams salt will convert 108 grams of silver into silver chloride and consequently .01 gram will precipitate $\frac{108 \times .01}{58.5} = .0184$ gram of silver.

16. But it is customary to make standard solutions of such a strength that one solution will be comparable with another, that is to say that the quantities of the *active constituents* in such solutions will be proportional to their chemical equivalents. Standard solutions, therefore, of common salt and of silver nitrate—(the example used above might be called an *empirical* standard solution)—will contain in a litre 35.5 grams of chlorine and 108 grams of silver respectively. So, taking one litre as the volume in which the substances are contained, standard solutions of hydrochloric acid, sulphuric acid, nitric acid, sodium hydrate, and potassium carbonate, will contain 1, 1, 1, 23, and 39 grams of hydrogen, of sodium and of potassium respectively. Such solutions are called **Normal Solutions** and a normal solution may be defined as *one containing the chemical equivalent of one gram of hydrogen per litre.*

17. For example:

Normal	HCl,	(molecular wt.	1 + 35.5,	*i.e.,*	36.5)	contains	36.5	grams per litre.
"	HNO_3,	(" "	1 + 14 + 48,	"	63)	"	63	" " "
"	KHO,	(" "	39.1 + 1 + 16,	"	56.1)	"	56.1	" " "
"	NaHO,	(" "	23 + 1 + 16,	"	40)	"	40	" " "
"	H_2SO_4,	(" "	2 + 32 + 64,	"	98)	"	$\frac{98}{2}$	" " "
"	H_3PO_4,	(" "	3 + 31 + 64,	"	98)	"	$\frac{98}{3}$	" " "
"	Na_2CO_3,	(" "	46 + 12 + 48,	"	106)	"	$\frac{106}{2}$	" " "
"	$AgNO_3$,	(" "	108 + 14 + 48,	"	170)	"	170	" " "
"	$HC_2H_3O_2$,	(" "	4 + 24 + 32,	"	60)	"	60	" " "

In the case of acids it will be seen that the quantities required for one litre of normal solutions are those that contain 1 gram of replaceable hydrogen ; in the examples of salts given—potassium and sodium hydrates, sodium carbonate and silver nitrate, *the chemical equivalents oj 1 gram of hydrogen* are potassium (39.1), sodium (23) and silver (108) ; quantities of these salts, therefore, are taken which will contain these amounts of their respective *active* constituents, which, in these cases, are the elements themselves. Solutions will be met with later on in which a *portion* only and not the whole of some particular element takes part in the reaction for which it is used and these cases will be considered and explained as they occur.

18. It will be seen from what has been said that any volume of a normal solution of an acid will be exactly neutralised by the *same* volume of a normal alkali. This will be made clearer by the following equations which represent the reactions that take place between the commoner acids and bases.

$$(a)\quad \underset{36.5}{HCl} + \underset{56.1}{KHO} = KCl + H_2O$$

$$(b)\quad \underset{2\times36.5}{2HCl} + \underset{106}{Na_2CO_3} = 2NaCl + H_2O + CO_2$$

$$(c)\quad \underset{98}{H_2SO_4} + \underset{2\times40}{2NaHO} = Na_2SO_4 + 2H_2O$$

$$(d)\quad \underset{98}{H_2SO_4} + \underset{106}{Na_2CO_3} = Na_2SO_4 + H_2O + CO_2$$

$$(e)\quad \underset{56.1}{KHO} + \underset{60}{HC_2H_3O_2} = KC_2H_3O_2 + H_2O$$

From these equations it is evident that 56.1 grams KHO, 40 grams NaHO, 53 grams Na_2CO_3, will neutralise 36.5 grams HCl, 63 grams HNO_3, 49 grams H_2SO_4, 60 grams $HC_2H_3O_2$, and, as these are the amounts contained in one litre of a normal solution of each, it follows that a litre or any fraction thereof of a normal alkali will exactly neutralise a litre or the same fraction thereof of any normal acid. So, therefore, if a litre of normal KHO was found to exactly neutralise a quantity of hydrochloric acid, this acid solution must have contained 36.5 grams HCl. Similarly, if a sample of dilute sulphuric acid required 80 c.c. of normal KHO (or normal NaHO, or normal Na_2CO_3) to neutralise it, it must have contained 80 × .049 grams H_2SO_4, each c.c. of normal alkali being capable of neutralising .049 gram H_2SO_4.

19. Standard acids are used for determining alkalies and *vice-versa*, but *normal* solutions are seldom employed being too concentrated to admit of accurate work. Some fraction of normal, as *half-normal*, or *decinormal*, or *centinormal* is more often used and the expressions $\frac{N}{2}$, $\frac{N}{10}$, $\frac{N}{100}$ indicate these strengths. An $\frac{N}{10}$ solution of hydrochloric acid will thus contain 3.65 grams HCl per litre and each c.c. will contain .00365 gram HCl. From the equations given it will be seen that this amount (1 c.c.) of hydrochloric acid is capable of neutralising .0056 gram potassium hydrate, .004 gram sodium hydrate, .0053 gram sodium carbonate, etc., and that 1 c.c. of decinormal sulphuric, nitric and acetic acids can also neutralise these amounts of the alkalies named. Conversely, 1 c.c. of any decinormal alkali will neutralise .00365 gram HCl, .0049 gram H_2SO_4, .0063 gram HNO_3, .006 gram $HC_2H_3O_2$.

20. As these standard solutions are continually being used for determining the amounts of free acid or alkali in solutions they may be conveniently summarised as follows.*

$\frac{N}{10}$ HCl
1 c.c. = .00365 gram HCl
= .0056 " KHO
= .0040 " NaHO
= .0053 " Na_2CO_3
= .0017 " NH_3

$\frac{N}{10}$ KHO
1 c.c. = .0056 gram KHO
= .00365 " HCl
= .0049 " H_2SO_4
= .0063 " HNO_3
= .0060 " $HC_2H_3O_2$

$\frac{N}{10}$ H_2SO_4
1 c.c. = .0049 gram H_2SO_4
= .0056 " KHO
= .0040 " NaHO
= .0053 " Na_2CO_3
= .0017 " NH_3

$\frac{N}{10}$ Na_2CO_3
1 c.c. = .0053 gram Na_2CO_3
= .00365 " HCl
= .0049 " H_2SO_4
= .0063 " HNO_3
= .0060 " $HC_2H_3O_2$

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* The sign of equality "=" is used with reference to standard solutions to signify that 1 c.c. *contains* so-many grams of the reagent, and also that 1 c.c. *will react with* so-many grams of the other substance named.

EXAMPLES OF VOLUMETRIC ANALYSIS.

21. Methods based on Neutralisation or Saturation. Alkalimetry; the determination of the strength of solutions of alkalies by titration with a standard solution of an acid.

A standard solution of an acid is added to a known quantity of the alkali under examination till the solution becomes neutral. This "end-point" is indicated by the change in colour imparted to certain vegetable colouring-matters added to the solution, which are extremely sensitive, yielding different tints according as the solution is alkaline or acid. From the number of c.c. of the acid used the amount of alkali present is found and the result given in *grams per litre.*

22. The indicators employed in alkalimetry and acidimetry are *litmus*, *phenolphthalein*, and *methyl-orange*. These react as under:

	With acids	*With alkalies*
Litmus	red	blue
Phenolphthalein	colourless	red
Methyl-orange	reddish pink	yellow

Litmus is affected by carbon dioxide and in the titration of a carbonate (which will evolve this gas) does not give a true indication of the end of the reaction until the carbon dioxide has been expelled by boiling.

Methyl-orange, on the other hand, is unaffected by carbon dioxide and is therefore specially useful for the titration of alkaline carbonates, no boiling being necessary. It, however, cannot be used in titrating organic acids.

Phenolphthalein is also affected by carbon dioxide but can be employed in the presence of organic acids. It cannot be used if ammonia is present.

23. Determination of the strength of a given solution of potassium hydrate by titration with $\frac{N}{10}$ H_2SO_4,(1) using methyl-orange as indicator.(2)

A known volume, say 10 c.c., is taken up with a pipette and placed in a beaker; water is added till there is about half-an-inch of liquid in the vessel together with a drop or two of methyl-orange. A burette is filled with $\frac{N}{10}$ H_2SO_4 and adjusted to the zero mark.(3) The beaker is placed on a sheet of white paper underneath the burette, which is clamped in a perpendicular position to its stand, and the acid run in very slowly, the contents of the beaker being stirred, or a circular motion imparted to them, until the change of colour of the methyl-orange from yellow to reddish pink indicates that the reaction(4) is completed. The number of c.c. of acid required is noted and the whole operation repeated once or twice until the end-point is accurately obtained. The strength of the solution of potassium hydrate is then calculated.

One example will illustrate how this is done; the method of calculation is equally applicable to subsequent volumetric experiments also. 10 c.c. of a solution of potassium hydrate, titrated with $\frac{N}{10}$ H_2SO_4, using methyl-orange as indicator, required (say) 30.1 c.c. of the acid for neutralisation:(5)

$$\therefore 10 \text{ c.c. of solution contain } 30.1 \times .0056 \text{ grams KHO}^{(6)}$$

$$\therefore 1 \text{ litre contains } 100 \times 30.1 \times .0056 \text{ grams KHO} = 16.856 \text{ grams KHO.}^{(7)}$$

---

(1) It is evident that to accurately weigh out the necessary amount of sulphuric acid (actual H_2SO_4), or of potassium or sodium hydrate, and make their solutions up to one litre is no easy matter as they are extremely hygroscopic and the weights taken would not be exact. Hydrochloric acid, being volatile, presents similar difficulties. Sodium carbonate can, however, be obtained of great purity and, being neither volatile nor hygroscopic, the required amount can be weighed with perfect accuracy and a standard solution obtained. With this solution it is easy to determine how far short of being "standard" the comparatively roughly made solutions of the acids may be and more water or more acid can be added to bring them to the "standard." So, by means of an acid "standardised" in this way, the strength of solutions of other alkalies can be found and water or the salt added until they, in turn, are standardised.

(2) As a caustic alkali, such as potassium hydrate, always contains a certain amount of carbonate it is necessary to use methyl-orange as indicator if accurate results are to be obtained. See remarks on indicators above.

(3) See remarks on filling and reading burettes, p. 2.

(4) See equation (*c*) on p. 4.

(5), (6), and (7). See foot of next page.

24. Determination of the strength of a given solution of sodium carbonate by means of $\frac{N}{10}$ H_2SO_4, using methyl-orange as indicator.

10 or 20 c.c. of the sodium carbonate solution are transferred to a beaker, a drop or two of methyl-orange added and, in a manner similar to that described in **23**, $\frac{N}{10}$ H_2SO_4 run in—a few c.c. at a time to begin with and then drop by drop as the reaction nears completion—till a permanent red colour is produced. The number of grams of sodium carbonate per litre are then calculated.

25. Determination of sodium carbonate, using litmus as indicator.

The process is carried out as described in the previous example but *the solution must be boiled to expel the carbon dioxide* which acts on the litmus, turning it red. The acid is added gradually until the colour changes from blue to a purple-red ; the solution is then boiled until the blue colour returns, more acid run in and the boiling repeated until a single drop of acid causes a *permanent red* colour, unchanged by further boiling. The strength of the sodium carbonate is calculated as in former examples.

26. Determination of caustic alkali and carbonate when mixed.

When sulphuric acid is added to a mixture containing both hydrate and carbonate of an alkali the reaction takes place in two stages ; first the hydrate and *half* the carbonate are neutralised according to the equations,

$$\begin{aligned} 2KHO + H_2SO_4 &= K_2SO_4 + 2H_2O \\ \text{and } 2Na_2CO_3 + H_2SO_4 &= 2NaHCO_3 + Na_2SO_4 \end{aligned}$$

half the carbonate becoming the bicarbonate. The bicarbonate is *not alkaline to phenolphthalein* so, if this indicator is added and such a mixture titrated with standard sulphuric acid, the phenolphthalein will become colourless when that stage in the neutralisation of the alkalies is reached represented by the expression,

$$\underbrace{2KHO + 2Na_2CO_3}_{\text{Mixture of hydrate and carbonate}} + 2H_2SO_4 = \underset{\substack{\text{Hydrate}\\ \text{neutralised.}}}{K_2SO_4} + \underset{\substack{\text{Half the carbonate}\\ \text{neutralised.}}}{Na_2SO_4} + \underset{\substack{\text{Half the carbonate}\\ \text{changed to bicarbonate.}}}{2NaHCO_3} + 2H_2O$$

But the bicarbonate ($NaHCO_3$) yields a yellow colour with methyl-orange, which indicator is therefore added at this stage and the titration with acid continued till the liquid becomes pink, shewing the completion of the reaction, $2NaHCO_3 + H_2SO_4 = Na_2SO_4 + 2H_2O + 2CO_2$. The results are readily calculated from the amounts of acid used, (*a*) to decolourise the phenolphthalein, which will be that required to neutralise *all* the caustic alkali and *one half* the carbonate present, and (*b*) to complete the second stage of the reaction, which will be that required to neutralise *half* of the carbonate. This latter number, if doubled, gives the volume of acid necessary to neutralise *all* the carbonate. The sum of (*a*) and (*b*) is the acid required to neutralise *all* the alkali present.

A numerical example will illustrate how the results of these titrations can be calculated. To 20 c.c. of a solution containing sodium carbonate and potassium hydrate, phenolphthalein is added and $\frac{N}{10}$ sulphuric acid run in till the solution is colourless. 10 c.c. of acid are required. On the addition of methyl-orange and further titration, 5 c.c. are found to be necessary for complete neutralisation.

Acid required for neutralisation of the caustic alkali and *half* the carbonate...... 10.00 c.c.
Acid required to complete the neutralisation, *i.e.*, to saturate *half* the carbonate.. 5.00 "

Total acid required for both caustic and carbonate .... 15.00 "

Acid required for *all* the carbonate $2 \times 5 = 10$ c.c.
∴ Acid required for the caustic $15 - 10 = 5$ c.c.

Hence 1 litre of solution contains—

$$\text{Potassium hydrate } \frac{1000 \times 5 \times .0056}{20} \text{ grams.}$$

$$\text{Sodium carbonate } \frac{1000 \times 10 \times .0053}{20} \quad \text{"}$$

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(5) The first titration is usually taken merely as a *guide* to the amount that can safely be added all at once in subsequent titrations, when the last few fractions of a c.c. must be added drop by drop with continued mixing between.

(6) See **20**.

(7) It is a useful exercise, as tending to a fuller understanding of the principles underlying the composition of normal solutions and of volumetric analysis generally, to calculate from the number of grams per litre determined in such experiments as the above *what fraction of normal* the solution, whose strength has just been ascertained, is ; in other words, how to express it in terms of N. Normal KHO contains 56 grams KHO per litre, while the above solution contains only 16.8. If x represents the coefficient of N that is required, then $56 : 16.8 = N : xN$

$$\therefore xN = \frac{N \times 16.8}{56}$$

$$\text{and } x = \frac{16.8}{56}$$

$$\text{The solution is } \frac{16.8}{56} N.$$

27. On completion of the foregoing experiments the student should determine by a similar method of procedure the strength of the following laboratory reagents, expressing the results in grams per litre : (8)

Potassium hydrate, using methyl-orange as indicator.
Potassium hydrate, " phenolphthalein " "
Sodium carbonate, " methyl-orange " "
Sodium carbonate, " litmus " "
The proportions of caustic alkali and carbonate in the potassium hydrate, (see **26**).
Ammonium hydrate, using litmus or methyl-orange as indicator.

28. Acidimetry; the determination of the strength of solutions of acids by titration with a standard solution of an alkali.

This is the converse of alkalimetry and what has been said about the estimation of alkalies applies equally to acidimetry. Using a decinormal solution of potassium hydrate and a suitable indicator the student should now determine the strength of the laboratory solutions of *hydrochloric acid*, *sulphuric acid*, *nitric acid* and *acetic acid*. For the titration of the last named, the indicator used should be phenolphthalein.

29. The determination of ammonia by what is known as "titrating back"

should also be done. A normal solution of this substance would contain 17 grams NH_3 per litre but would lose its strength if left exposed to the air. A half normal solution is comparatively stable and a decinormal one keeps well. In determining free ammonia in this way a *known* amount of standard acid, *in excess of what will be required to neutralise the ammonia*, is added and the *excess* titrated with standard alkali and methyl-orange as indicator.

From this the weight of NH_3 can be readily calculated. For example ; to 10 c.c. of a solution of ammonia of unknown concentration are added 50 c.c. of $\frac{N}{10}$ sulphuric acid(9) and the *excess* of sulphuric acid titrated with $\frac{N}{10}$ potassium hydrate (using methyl-orange as indicator) of which 20 c.c. are required to neutralise the excess of $\frac{N}{10}H_2SO_4$. $\therefore$ 50 – 20, *i.e.* 30 c.c. is the amount of $\frac{N}{10}$ H_2SO_4 required to neutralise the sample of ammonia.(10)

As each c.c. of $\frac{N}{10}H_2SO_4$ is equivalent to .0017 gram of NH_3

$\therefore$ 1 litre of the ammonia solution contains

$$\frac{1000 \times 30 \times .0017}{10} \text{ grams ammonia.}$$

Standard acids and alkalies can be used for a number of other determinations.

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(8) As the ordinary burette is seldom graduated for use with more than 50 c.c. there will often be too little standard solution contained in it to complete the reaction desired. When this is the case it is best to dilute the quantity of original solution taken with water *to a known volume* and with a pipette to remove an aliquot portion for each titration. For example, if the 10 (or 20) c.c. of these laboratory solutions that are taken for each analysis consume more than a buretteful of standard acid it is best to *at once* measure out a fresh 10 (or 20) c.c. of solution and *make it up to 50 c.c.* by running into it the necessary amount of water from a clean burette and thoroughly mixing. Portions of this diluted sample are then pipetted out into a beaker and titrated. It is a simple matter to know how much *of the original sample* is in each aliquot portion taken. In the above supposititious case if 10 c.c. of the original solution are made up to 50 c.c. and portions of 10 c.c. used for each titration, each portion will contain one-fifth of 10 c.c., namely 2 c.c. of the original substance.

(9) It is presumed in this illustration that 50 c.c. of acid is *more than enough* to neutralise the ammonia in the sample.

(10) The acid and the alkali here used are each decinormal and therefore 1 c.c. acid = 1 c.c. alkali. Were they different it would be the number of c.c. of acid equivalent to the amount of alkali added in the titration that would be deducted from the original quantity used.

30. To estimate a carbonate, insoluble in water, by dissolving it in an excess of standard acid and titrating back.

2 grams of a sample of "precipitated chalk" are weighed on a watch-glass and transferred to a beaker, carefully washing the glass free of all adhering powder and adding from 50 to 100 c.c. of water. Into the water containing the carbonate in suspension is run *an excess* of normal HCl till all effervescence ceases and the amount used noted. Two or three drops of methyl-orange are added and the excess of acid titrated with normal KHO. If the amount of normal HCl added in the process of solution is 60 c.c. and 20.5 c.c. normal KHO are required to neutralise the *excess* of acid,

$\therefore$ 60 − 20.5 = 39.5 c.c.(11) is the amount of normal HCl that reacted with the sample of chalk.

As 1 c.c. normal HCl is equivalent to .05 gram $CaCO_3$(12)

$\therefore$ the sample contains 39.5 × .05 = 1.975 grams $CaCO_3$.

31. Determination of the "temporary hardness" of water by titration with standard acid.

Temporary hardness in water is due to the presence in small quantities of carbonates of calcium (or magnesium) rendered soluble by carbon dioxide. The amount is usually so little that if normal or even decinormal acid were used to decompose them the error would be very great owing to the small quantities required for the titration. A much less concentrated acid is employed, therefore, $\frac{N}{50}$ being a suitable strength. This can be prepared by the student by taking 20 c.c. of the normal hydrochloric acid used in the previous exercise and making that volume up to 1000 c.c. with water. The determination may then be done in two ways :

(*a*) To 100 c.c. of the "hard" water under examination are added two or three drops of methyl-orange and $\frac{N}{50}$ HCl run in till the end-point is indicated by the solution turning red.

(*b*) In a manner similar to **30** an *excess* of acid may be added and the excess estimated by $\frac{N}{50}$ KHO, which can be prepared from the normal KHO in the same way as the $\frac{N}{50}$ HCl is made from the normal acid.

From the amount of acid required to react with the carbonate the "degree of hardness" can be calculated, a degree of hardness being taken as 1 part $CaCO_3$ per 100,000 of water. Each c.c. of $\frac{N}{50}$ HCl is equivalent to .001 gram $CaCO_3$. So, if the sample required 20 c.c. $\frac{N}{50}$ HCl to decompose the $CaCO_3$ then the 100 c.c. sample will contain 20 × .001 gram $CaCO_3$ = .02 gram $CaCO_3$.

$\therefore$ 100,000 parts will contain 1000 × .02 = 20 grams $CaCO_3$.

This water would be said to have a hardness of 20 degrees.

32. Methods based on Oxidation.

Quite a number of oxidising agents are employed in the form of standard solutions for determining the amounts of substances that are capable of being oxidised quantitatively. One of the most useful solutions of this kind is potassium permanganate, which has the additional advantage of *requiring no indicator other than itself.* In the process of oxidising it becomes *reduced* to a salt of manganese which is practically colourless and the slightest trace of any permanganate over and above what is required to complete the reaction imparts a pink tinge to the solution. It is used for estimating iron, and for oxalic acid and oxalates ; indirectly it can be used for the determination of any base capable of yielding an insoluble oxalate.

33. In making a normal solution of permanganate only one fifth of the molecular weight in grams is taken in a litre of water. The definition of a normal solution previously given states that a litre of such a solution is to contain the *chemical equivalent* of 1 gram of hydrogen. In permanganate the oxygen is the *active* constituent so such a quantity of the salt is used as will contain 8 *grams of oxygen available for oxidising purposes*, 8 grams of oxygen being equivalent to 1 gram of hydrogen. If the formula of the permanganate—doubled to allow of what follows being expressed—be divided

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(11) See latter part of note 10.

(12) This is readily seen from the equation

$$\begin{array}{ll} CaCO_3 & + 2\,HCl = CaCl_2 + H_2O + CO_2 \\ \underbrace{40+12+48}_{100} & + 2 \times 3.65 \\ i.e.\ 50 & + 36.5 \end{array}$$

Normal HCl contains 36.5 grams per litre, therefore each c.c. can dissolve .05 gram $CaCO_3$.

up to represent the oxides into which it might be resolved in process of performing its oxidising function it can be written thus, $\underset{94}{K_2O}$, $\underset{142}{2MnO}$, and $\underset{80}{O_5}$. Oxidation with permanganate in volumetric analysis requires the presence of (preferably) free sulphuric acid,(13) the decomposition products of the salt forming with it potassium sulphate and manganese sulphate (otherwise the oxide of the latter will precipitate), while the proportion of oxygen which is set free oxidises whatever oxidisable body it may be in contact with, thus,

$$\underset{2\times158}{2KMnO_4} + 3H_2SO_4 = K_2SO_4 + MnSO_4 + 3H_2O + \underset{80}{O_5}$$

There are thus 80 grams of available oxygen in 316 of permanganate, or 40 in the formula-weight, $KMnO_4$ (158). How many grams of this salt, then, will it be necessary to have contained in one litre in order to obtain a normal solution? If there are forty grams of available oxygen in 158 grams of permanganate, $\frac{158 \times 8}{40} = 31.6$ grams will contain the necessary 8 grams of available oxygen; normal permanganate, therefore, contains 31.6 grams of the salt per litre and a decinormal solution will contain 3.16 grams. Before use this solution will have to be accurately standardised, just as the normal sulphuric acid was standardised against pure sodium carbonate. In the case of permanganate solution this is done with pure iron wire or with pure crystallised oxalic acid—the method of procedure is the same as in the following exercises, in which examples it will be presumed that the standard permanganate employed is exactly normal or decinormal, or such fraction of normal as it is stated to be.

34. Standard permanganate has its principal application in determining iron, by its power of converting ferrous salts into ferric salts; and in determining free oxalic acid, which is broken up by it into water and carbon dioxide. The nature of these reactions can best be seen thus:

(*a*) $2KMnO_4 + \underset{10(FeO\,.\,SO_3)}{10FeSO_4} + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + \underset{5(Fe_2O_3\,.\,3SO_3)}{5Fe_23SO_4} + 8H_2O$

or, expressing oxidation only, $10FeO + O_5 = 5Fe_2O_3$; that is to say, 560 grams of iron are oxidised by 80 grams of oxygen.

(*b*) $2KMnO_4 + \underset{\text{(oxalic acid)}}{5H_2C_2O_4} + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$

or, expressing oxidation only, $5H_2C_2O_4 + O_5 = 5H_2O + 10CO_2$; that is, 450 grams oxalic acid are oxidised by 80 grams of oxygen. Thus 8 grams of oxygen are equivalent to 56 grams of iron and to 45 grams of anhydrous oxalic acid. As a decinormal solution of permanganate contains .8 gram available oxygen per litre (see ante), each c.c. of it will be the measure of .0056 gram Fe and of .0045 gram $H_2C_2O_4$.(14)

35. Determination of iron in a solution of ferrous sulphate or other ferrous salt.

A measured quantity of the ferrous solution is transferred to a flask or beaker, and diluted somewhat with distilled water,(15) about half its volume of dilute sulphuric acid added, and $\frac{N}{10}$ $KMnO_4$ run in, the contents of the beaker being thoroughly mixed. The titration is continued until the solution of permanganate produces a faint permanent pink best seen if the containing vessel is placed on a white tile or sheet of paper. Knowing that each c.c. of $\frac{N}{10}$ $KMnO_4$ is equivalent to .0056 gram of iron, the quantity of ferrous salt present—*whatever salt it may be*(16)—can readily be calculated; for every 56 grams of iron can yield 56 + 32 + 64 = 152 grams $FeSO_4$(17) or 278 grams of $FeSO_47H_2O$, the crystallised salt. So for any other ferrous salt.

An example will illustrate the simplest method of making such a calculation:—10 c.c. of a solution of ferrous sulphate required 24.8 c.c. of $\frac{N}{10}$ $KMnO_4$ for oxidation;

$$\therefore \text{10 c.c. of solution contains } 24.8 \times .0056 \text{ gram Fe} = .1388 \text{ gram Fe.}$$

and $\underset{56}{Fe} : \underset{152}{FeSO_4}$ = amount of Fe found : amount of $FeSO_4$ to which that quantity of Fe is equivalent.

$$\therefore \text{this amount of } FeSO_4 = \frac{.1388 \times 152}{56} = .3767 \text{ gram in 10 c.c.}$$
$$= 37.67 \text{ grams per litre.}$$

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(13) In all titrations with permanganate the solution must be acidified with sulphuric acid. Nitric acid should not be present and hydrochloric acid is liable to become oxidised by the permanganate and to evolve chlorine. Organic matter must not be present.

(14) Crystallised oxalic acid is $H_2C_2O_42H_2O$, hence the equivalent in it would be .0063 gram.

(15) Ferrous salts rapidly oxidise in solution especially if the water has not been freshly boiled or distilled and allowed to become *perfectly cool.*

(16) The term "oxidation" is applicable not only to cases where the proportion of actual oxygen is increased but also to salts with no oxygen in their composition. When ferrous chloride, ($Fe''Cl_2$), becomes ferric chloride, ($FeCl_3$), it is said to have been oxidised. The word is used to express the change that takes place in a substance analogous to the conversion of a lower into a higher oxide.

(17) Atomic weights used here are Fe, 56; S, 32; O, 16; K, 39; Mn, 55.

36. Determination of iron in ferric sulphate or other ferric salt.

From what has been said it will be seen that permanganate only affects iron salts when they are in the *ferrous* condition: this, however, does not prevent its use for estimating *ferric* salts also, for these can be *reduced* to ferrous salts, the iron then determined by oxidation with standard permanganate as in the previous example, and the amount thus found "calculated to" the particular ferric salt.

To determine, therefore, the amount of (say) "iron-alum" ($\text{K Fe}''' 2\text{SO}_4 12\text{H}_2\text{O}$) in a solution of that salt, transfer some 20 or 30 c.c. to a beaker or an Erlenmeyer flask, add water and about 10 c.c. of concentrated sulphuric acid. A few fragments of metallic zinc are added and the flask set aside till the evolution of hydrogen ceases and the zinc is all dissolved. The solution may require to be heated to effect the complete solution of the zinc. A portion of the hydrogen at the moment of its liberation reacts with the ferric sulphate which becomes *reduced* to ferrous sulphate. This reduction must be complete and to test if this is so a drop is removed on the end of a glass rod, placed on a white surface, such as the lid of a porcelain crucible, and a drop of ammonium or potassium sulphocyanate added. If any ferric salt remains a red colour will be produced and further reduction with zinc and acid must be resorted to. When free from ferric salt, that is, when it gives no distinct colour with sulphocyanate, the flask is cooled under the tap and at once titrated with $\frac{N}{10}\text{KMnO}_4$.

The amount of ferric salt is then calculated as follows. Let 20 c.c. be the volume of solution taken for the determination and after reduction with zinc and sulphuric acid 45 c.c. $\frac{N}{10}$ KMnO_4 are found necessary to oxidise it. Then 20 c.c. of sample will contain $45 \times .0056$ gram Fe(18) = .252 gram Fe.

To calculate this to iron-alum,

$$\underset{56}{\text{Fe}} : \underset{503}{\underbrace{\text{KFe2SO}_4 12\text{H}_2\text{O}}} = \underset{.252}{\text{amount of Fe found}} : \text{grams KFe2SO}_4 12\text{H}_2\text{O}$$

$$\therefore \text{ amount of KFe2SO}_4 12\text{H}_2\text{O in 20 c.c.} = \frac{.252 \times 503}{56} \text{grams.}$$

$$= 2.26 \text{ grams.}$$

$$\text{Hence, a litre contains } \frac{2.26 \times 1000}{20} \text{grams.}$$

37. Determination of ferrous and ferric salts when mixed.

(*a*) *Total Iron.* A portion of the solution—of known volume—is reduced by means of zinc and sulphuric acid and treated as described in **36**.

(*b*) *Iron in the form of ferrous salt.* In another portion—of equal volume—(19) of the solution the ferrous iron is determined as described in **35**.

Let the mixture be one of ferrous sulphate and ferric sulphate, then the calculation of the composition of the solution is made as follows:

From (*a*) is obtained the total iron.............................. x.
From (*b*) is obtained that present as ferrous salt.................. y.
∴ Fe in (x) − Fe in (y) = Fe which is present as ferric salt.... z.

y and z are then calculated to FeSO_4 and to $\text{Fe}_2 3\text{SO}_4$ respectively by the arithmetical process described in former examples.

38. Determination of the strength of a solution of permanganate by iron wire.

About .2 gram of pure iron wire is weighed carefully, transferred to an Erlenmeyer flask and about 100 c.c. of dilute sulphuric acid added. The flask and contents are placed on a sand-bath and allowed to simmer till the wire has completely dissolved: a few minute particles of carbon often remain but these will not interefere with the subsequent process. A filter-funnel may, with advantage, be inserted in the neck of the flask as it will prevent the access of air while not interfering with the escape of the hydrogen. The flask is cooled under the tap, some distilled water added if need be, and the ferrous sulphate solution titrated at once with the permanganate solution whose strength is wanted. The calculation can be done as follows:

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(18) It is plain that if 1 c.c. $\frac{N}{10}$ KMnO_4 is equivalent to .0056 grams Fe, it must also be equivalent to .0503 gram $\text{KFe2SO}_4 12\text{H}_2\text{O}$, to .008 gram Fe_2O_3, to .0072 gram FeO, to .0152 grams FeSO_4, and so on. The same result as has been got above after a comparatively lengthy explanation, *viz.*, 2.26 grams, would have been obtained had the number of c.c. permanganate used, *viz.*, 45, been multiplied by .0503, which is the fraction of the molecular wt. of iron-alum equivalent to 1 c.c. $\frac{N}{10}\text{KMnO}_4$.

(19) It is evident that the only reason for suggesting the use of similar volumes of the solution of mixed salts is to simplify the subsequent calculation, and to allow of the figure obtained from (*b*) being subtracted directly from (*a*), these being the amounts in *equal* volumes; z will therefore be the amount of iron present as ferric salt in a similar volume. In practice it would not always be convenient to take the same amounts for each determination, particularly if the samples were solids. The results of (*a*) and (*b*) must necessarily be brought to the same denomination before their difference can be ascertained.

If .2 gram of iron is found to require 50 c.c. $KMnO_4$ for oxidation, and it is known by what has been explained earlier that 31.6 grams $KMnO_4$ can oxidise 56 grams of iron, then the amount of $KMnO_4$ that can oxidise .2 gram must be $\frac{31.6 \times .2}{56}$, *i.e.* $\frac{31.6}{280}$ gram, the amount in 50 c.c.

$\therefore$ 1 litre of the permanganate will contain $\frac{31.6 \times 1000}{280 \times 50}$, *i.e.* 2.26 grams.

As 31.6 grams permanganate per litre constitutes a normal solution, the strength of the one under examination must be $\frac{2.26}{31.6}$ of normal, namely $\frac{N}{14}$ approximately.

Another method of reasoning, which leads to the same result, is :—50 c.c. of the unknown permanganate are found to oxidise .2 gram of iron ; and it is known that, as each c.c. of normal permanganate is equivalent to .056 gram of iron, 50 c.c. of such a solution must be capable of oxidising $50 \times .056$, namely 2.8 gram of iron ; therefore the solution must be $\frac{.2}{2.8}$ of normal, *i.e.* $\frac{N}{14}$.

39. Determination of oxalic acid by titration with standard permanganate.

From what has been said in **34** it will be seen that oxalic acid is readily converted into carbon dioxide and water by solutions of permanganate.

To perform this estimation the oxalic acid solution is acidified with sulphuric acid, *gently heated* to a temperature of about 60° C.* and the permanganate run cautiously in from a burette. An appreciable time is necessary for the oxidation of the oxalic acid and consequent reduction of the permanganate, so the pink colour does not disappear as rapidly as in the titration of ferrous salts. Especially is this the case towards the end of the reaction, and great care must be exercised at this stage, the permanganate being added cautiously and the solution allowed to stand to permit of the colour being discharged otherwise the end-point may be overstepped. At the first sign of a *permanent* pink after the solution has stood for a minute or so the titration may be considered finished and one or two more titrations should be done till the student is satisfied that he has hit off the end-point exactly. Each c.c. of $\frac{N}{10}$ $KMnO_4$ oxidises .0045 gram anhydrous $H_2C_2O_4$.(19) The amount of oxalic acid present can easily be calculated.

40. Determination of a soluble oxalate.

On the addition of sulphuric acid to a soluble oxalate, oxalic acid is set free : the above estimation can therefore be done in the same way as described in **39**, the amount of oxalic acid found being calculated to the particular oxalate employed.

41. Determination of metals that yield insoluble oxalates.

Taking calcium as an example of a metal yielding an insoluble oxalate, the metal is completely precipitated as oxalate, the precipitate washed free from all soluble matter, redissolved in acid and the liberated oxalic acid titrated with standard permanganate. From the numerical relation between $H_2C_2O_4$, the calcium oxalate CaC_2O_4 and the actual salt of calcium employed, the desired result can be calculated.

To perform the estimation, a known quantity of a soluble calcium salt is taken, diluted with water, ammonia added till the solution smells strongly of that reagent and the liquid heated to boiling. A warm solution of ammonium oxalate is then added, the mixture boiled for a few minutes and the precipitated calcium oxalate allowed to settle. The supernatant liquid is decanted through a filter, the precipitate washed once or twice by decantation and transferred to the filter where it is washed with hot water till the filtrate gives no reaction when tested for oxalic acid. The precipitate is best transferred to the flask in which the titration is to be performed by placing the funnel in the mouth of the flask, puncturing the apex of the filter and washing it through with a fine jet of water from a wash-bottle. Any precipitate that remains adhering to the paper is dissolved off with *a little* hot hydrochloric acid, followed by more washing down with hot water. In this way every trace of calcium salt is transferred to the flask. Any precipitate in the flask that has not been dissolved by the acid which was poured on the filter is now treated with the *minimum amount of hydrochloric acid that will effect its solution*—and no more.(20) Sulphuric acid is now added, the mixture heated to about 60° C. and, *without further delay*, titrated with standard permanganate. The number of c.c. of permanganate required gives the amount of oxalic acid that went to form the insoluble CaC_2O_4, from which the calcium is calculated.

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* It is possible to insert the hand into water at 60° but not to retain it there with any degree of comfort. The temperature required for the experiment can therefore be approximately guaged when the beaker or flask containing the solution can be grasped firmly in the hand and held for a space of about two seconds only.

(19) See note 14.

(20) As each c.c. of $\frac{N}{10}$ $KMnO_4$ is equivalent to only .0045 gram $H_2C_2O_4$ (and consequently to .0064 gram CaC_2O_4) it would be more satisfactory at this stage to dilute the solution obtained as above to a known volume and remove an aliquot portion for titration with the permanganate in the presence of sulphuric acid. See also note 8.

42. The student should now apply the knowledge and experience gained of the uses of standard permanganate to the determination of the strength of certain of the laboratory reagents. For example: (*a*) The amount of ferrous sulphate in the laboratory solution of that salt. (*b*) The proportions of *ferrous* and *ferric* salts in it. (*c*) The strength of the ammonium oxalate. (*d*) The amount of calcium chloride in the laboratory solution. (*e*) The strength of the oxalic acid.

43. Decinormal potassium bichromate.

Standard solutions of potassium bichromate are frequently employed in place of permanganate especially for the estimation of iron; they cannot be used, however, for titrating oxalic acid. Titrations with bichromate can be done in the presence of hydrochloric acid, which acid is undesirable when permanganate is used. Estimations done with bichromate require an *outside indicator*, the one used being a *freshly prepared* solution of potassium ferricyanide which yields a blue colouration with ferrous salts but not with ferric. The absence of the blue colour, when a drop of the solution being examined is brought in contact with a drop of the ferricyanide placed on a white surface, indicates that the oxidation is complete.

The reaction between potassium bichromate and a ferrous salt can be expressed thus,

$$6Fe''SO_4 + 7H_2SO_4 + K_2Cr_2O_7 = 3Fe_2'''3SO_4 + K_2SO_4 + Cr_23SO_4 + 7H_2O$$

or, $6FeO$ take from the bichromate only O_3 and yield $3Fe_2O_3$.

The action of the *oxygen* on the ferrous salt can also be represented in this way,

$$\underset{6[FeO.SO_3]}{6Fe''SO_4} + 3H_2SO_4 + O_3 = \underset{3[Fe_2O_33SO_3]}{3Fe_2'''3SO_4} + 3H_2O$$

In order to ascertain how much bichromate is required to make a litre of a normal solution, an argument similar to that employed under normal permanganate will suffice. If the formula of potassium bichromate is dissected it may be written K_2O, 94; Cr_2O_3, 152; and O_3, 48; molecular weight, 294. Therefore, as 294 grams bichromate contain 48 grams of *available* oxygen, the weight of bichromate necessary to yield a normal solution(21) when contained in a litre of water will be $\frac{294 \times 8}{48}$, *i.e.* 49 grams. A decinormal solution, consequently, contains 4.9 grams $K_2Cr_2O_7$ per litre and each c.c. will oxidise .0056 gram of iron in combination as a ferrous salt to the ferric condition. Such a standard solution may be conveniently labelled "$\frac{N}{10}$ $K_2Cr_2O_7$; 1 c.c. = .0056 gram Fe.".

44. Determination of ferrous sulphate by decinormal potassium bichromate.

The general directions given in ***35*** are followed with this difference that in titrations with bichromate an indicator is required. For this purpose a *fresh* solution of potassium ferricyanide is made by dissolving a few crystals of the salt in water and a number of drops of this are "spotted" over the surface of a clean piece of white porcelain, such as a crucible lid or an inverted basin. From time to time a *drop* of the reacting solution is removed and the indicator touched with it. As long as any blue colour is produced the oxidation is incomplete and the addition of bichromate is continued till a drop of the solution no longer causes any change in the ferricyanide. The reaction is now complete, all the ferrous salt having been converted into ferric salt. From the amount of original substance taken for analysis and the number of c.c. of $\frac{N}{10}$ bichromate used the quantity of ferrous sulphate can be calculated.

The first few titrations with bichromate will, of necessity, be inaccurate owing to the removal of some of the salt during the "spotting" process. The best method of procedure is to rather overshoot the end-point to begin with, ascertaining in this way the number of c.c. that may safely be added at once and running this amount in before beginning to take any out with the glass rod. The last few drops can then be added cautiously, testing for the end-point after every small addition.

45. Determination of the strength of the laboratory ferric chloride solution by standard bichromate.

As this reagent usually contains free hydrochloric acid the permanganate method is not so applicable to its estimation as titration with standard bichromate. The procedure is the same as detailed in ***44***, after the ferric chloride has been reduced to ferrous chloride in the manner described in ***46***.

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(21) By definition, one containing 8 grams of available oxygen, the chemical equivalent of 1 gram of hydrogen.

46. Determination of ferrous and ferric salts in a mixture by standard bichromate.

This is done as described in **37** and **44**. Either zinc and hydrochloric acid or stannous chloride can be used for reducing the ferric salt previous to titration with bichromate: in inexperienced hands the former works best though it is slower and introduces a salt of zinc into the solution which is apt to interfere with the action of the ferricyanide indicator. The reduction is carried out as in **36**.

If the latter method is employed sufficient stannous chloride must be added to complete the reaction $2Fe'''Cl_3+SnCl_2=2Fe''Cl_2+SnCl_4$, but the end-point of the reduction cannot be tested for by potassium sulphocyanide as in **36**, so the addition of a *slight excess* of stannous salt is unavoidable. The excess must afterwards be removed by precipitation with mercuric chloride or it will react with the bichromate. To prepare the solution for titration, acidify with concentrated hydrochloric acid, heat to boiling and add about 2 c.c. of the laboratory stannous chloride, boil and add more reagent little by little, gently boiling all the time, till the solution is colourless: this may take some time. When this point is reached pour in *quickly* a larger quantity of mercuric chloride solution than it is thought will be required to precipitate the excess of stannous salt. If all has gone well a *white* precipitate of mercurous chloride will form which will not interfere with the subsequent titration with bichromate. The reaction may be expressed thus, $SnCl_2+2HgCl_2=SnCl_4+\mathbf{2HgCl}$; but if sufficient mercuric chloride is not added *at once* then the reaction $\mathbf{2HgCl}+SnCl_2=SnCl_4+\mathbf{2Hg}$ will occur and the precipitate will be gray or black. If this takes place there is no remedy but to repeat the analysis from the beginning. The results of the experiment are calculated as in **37**.

47. Determination of the strength of a solution of potassium bichromate by means of iron wire.

Apply the principles contained in **38, 43** and **44,** and from the results obtained calculate what is the strength of the potassium bichromate in terms of normal.

48. Standard iodine solution and its uses.

Iodine in the presence of water is capable of oxidising a number of substances quantitatively, the iodine becoming hydriodic acid (or an iodide). As the smallest trace of *free* iodine imparts a blue colour to solutions of starch the end-point of the reaction can be clearly obtained.(22) Estimations are done *directly* with standard solutions of iodine, or *indirectly* by determining the amount of *free* iodine that the body liberates from combination. Free iodine is capable of very accurate determination by means of sodium thiosulphate, and these two reagents in conjunction find numerous applications in analytical work.

49. Decinormal iodine.

12.7 grams of pure iodine are weighed out accurately and transferred to a litre flask. Water is poured in and about 20 grams of pure potassium iodide added,(23) the whole mixed thoroughly till solution is complete and the flask filled up to the litre mark. This solution, if correct, will contain .0127 *gram iodine per c.c.*

50. Decinormal sodium thiosulphate.

The quantity of *anhydrous* sodium thiosulphate required for a litre of a normal solution will be seen from the equation expressing the reaction between this salt and free iodine,

$$\underbrace{2Na_2S_2O_3}_{2\times158} + \underbrace{I_2}_{2\times127} = 2NaI + \underbrace{Na_2S_4O_6}_{\text{(sodium tetrathionate)}}$$

Thus, a normal solution of thiosulphate contains 158(24) grams per litre, a decinormal one 15.8.(25) *Each c.c. will be equivalent to* .0127 *gram iodine.*

51. Determination of iodine by titration with $\frac{N}{10}$ thiosulphate.

A known volume of a solution of iodine is placed in a beaker—resting on a white surface—and diluted to a convenient bulk with water. Standard thiosulphate is run in slowly, the solution being kept well mixed, until the colour of the iodine *almost* disappears. A few drops of starch(26) solution are now added causing a blue colour, and the thiosulphate added drop by drop till the complete discharge of the blue colour indicates that the reaction is at an end. The quantity of iodine in the sample is readily calculated. The converse of this should be done by the student, namely, delivering the standard iodine solution from a burette into a solution of thiosulphate containing a few drops of clear starch solution. The appearance of a permanent blue colour indicates the presence of the smallest excess of iodine.

(22) This blue coloured substance is usually known as iodide of starch: recent researches, however, point to it not being a chemical compound but a solid solution of iodine in starch.

(23) Iodine is sparingly soluble in water but readily soluble in a solution of potassium iodide. It dissolves freely in alcohol also, yielding "tincture of iodine."

(24) Crystallised sodium thiosulphate is $Na_2S_2O_35H_2O$, having a molecular weight of 248. In making the solution, therefore, 24.8 grams of the *crystallised* salt are taken.

(25) It will be observed that 1 litre of a normal solution of the salt contains the whole molecular weight in grams: it is evident from the equation that this amount is the chemical equivalent of 127 grams of iodine and consequently of 1 gram of hydrogen.

(26) Starch solution does not keep well and should always be freshly prepared. This is best done by grinding a few grams of white starch with water in a small mortar to form a milky paste, pouring this into a comparatively large amount of *boiling* water and then adding about twice the volume of cold water to the mixture. The solution is allowed to settle and the clear liquid poured off for use.

52. Determination by direct titration with standard iodine.

Solutions of hydrogen sulphide, of sulphur dioxide, of arsenious salts and of antimonious salts are oxidised by iodine in aqueous solution according the equations,

(*a*) $$\underbrace{H_2S}_{34} + \underbrace{I_2}_{2\times127} = 2HI + S$$

(*b*) (27)$$\underbrace{As_2O_3}_{198} + \underbrace{2I_2}_{4\times127} + 2H_2O = 4HI + As_2O_5$$

(*c*) $$\underbrace{Sb_2O_3}_{288} + \underbrace{2I_2}_{4\times127} + 2H_2O = 4HI + Sb_2O_5$$

(*d*) $$\underbrace{SO_2}_{64} + \underbrace{I_2}_{2\times127} + 2H_2O = 2HI + H_2SO_4$$

127 grams of iodine are thus equivalent to 17 grams of hydrogen sulphide, to 49.5 grams arsenic trioxide, to 72 grams antimony trioxide, and to 32 grams sulphur dioxide. 1 c.c. of a decinormal solution of iodine is therefore equivalent to .0017 gram H_2S, .00495 gram As_2O_3, .0072 gram Sb_2O_3 and .0032 gram SO_2. It is sometimes advisable to use solutions of less concentration than decinormal: twentieth normal or fiftieth normal are often employed. In the first of the examples that follow, a fiftieth normal solution admits of more accurate determinations being made. The student should try to become familiar with the conception of normal solutions by writing out what 1 c.c. of $\frac{N}{50}$ iodine would be equivalent to in the above reactions.

53. Determination of hydrogen sulphide in aqueous solution by standard iodine.

When solutions of hydrogen sulphide are *sufficiently dilute* the reaction between the hydrogen sulphide and iodine takes place according to the equation above, but if the solutions contain more than .04 per cent. *by weight* the change may not take place exactly as represented and therefore the method is useless. A sufficiently weak solution of the hydrogen sulphide can, however, be readily prepared by making up a definite volume of the hydrogen sulphide water to a known volume with air-free water. Even at best the method of analysis is not free from error as loss occurs by escape of the H_2S gas into the air and by oxidation.

A known volume of the laboratory solution of hydrogen sulphide is diluted with distilled water, starch added as indicator and the standard iodine solution run in. From the amount used before the permanent blue tinge is produced the quantity of hydrogen sulphide can be calculated.

A more accurate method is to add to a known volume of the standard iodine a measured quantity of the hydrogen sulphide solution *all at once* and to determine the *excess* of iodine by titration with thiosulphate. Examples of this method are given later.

54. Determination of arsenic by standard iodine.

The equation given in **52** shews how iodine in the presence of water oxidises arsenious oxide to arsenic oxide(28). To a known amount of a solution of arsenious oxide, or sodium arsenite, is added enough *bicarbonate* of sodium(29) to neutralise the arsenious oxide and ensure also a considerable excess of alkali in the solution. A few drops of starch are added and standard iodine run in until a permanent blue colour is produced. From the iodine used the amount of arsenic is calculated.

55. Determination of antimony in "Tartar-emetic" by standard iodine.

Equation (*c*) **52** represents the reaction that take places between antimony oxide (and its salts) and a solution of iodine. The quantity of $K(SbO)C_4H_4O_6$ present in a solution can be determined, therefore, by titration with standard iodine in the presence of an excess of sodium bicarbonate. Were it desired to estimate antimony oxide it would be first dissolved in tartaric acid and pure $NaHCO_3$ added before titration.

56. Determination of sulphur dioxide in aqueous solution by standard iodine.

As will be seen from equation (*d*) this can be done precisely in the same manner as hydrogen sulphide was estimated. The solutions must be very dilute. A more accurate method is described further on, **60**.

(27) See note (1) on page 8 of Qualitative Analysis.

(28) If A_2O_5 is present and the *total* arsenic is wanted it must be reduced to As_2O_3 by means of SO_2, the excess of SO_2 boiled off and the solution titrated with standard iodine.

(29) The solution must be alkaline in order to absorb the hydriodic acid produced in the subsequent reaction; see equation (*b*) of **52** Neither caustic alkali nor normal carbonate can be used as they would react with the free iodine. See also note (33).

57. *Determination of tin.*

Iodine and stannous chloride react in solution thus, $\underset{118+71}{SnCl_2} + \underset{2\times127}{I_2} = SnCl_2I_2$, *two* atoms of iodine being the measure of, or equivalent to *one* atom of tin. If metallic tin is given for analysis it must first be dissolved in hydrochloric acid, some $KNaC_4H_4O_6$ (Rochelle-salt) added and then sodium bicarbonate in excess before titration with standard iodine and starch.

58. *Determination by titrating the excess of iodine added with standard sodium thiosulphate.*

Both hydrogen sulphide and sulphur dioxide can be more accurately determined by adding a known volume of their diluted solutions to an excess of standard iodine solution—also of known volume—and ascertaining the amount of iodine not used up in the reactions by titration with standard thiosulphate as described in ***51***.

59. *Determination of chlorine in chlorine-water by iodine and thiosulphate.*

To a known volume of *dilute* chlorine-water is added an *excess* of potassium iodide; the solution thoroughly mixed and the liberated iodine determined by starch and thiosulphate. Every 35.5 grams of chlorine liberate 127 grams of iodine from the potassium iodide; from this the chlorine can be calculated.

60. *Determination of sulphur dioxide in a sulphite by iodine and thiosulphate.*

To a known volume of the sulphite solution is added an excess of standard iodine—also of known volume. The excess of iodine is titrated with starch and thiosulphate and the difference between the amount so found and the total iodine added is the proportion of iodine that has taken part in the reaction,

$$Na_2SO_3 + I_2 + H_2O = 2HI + Na_2SO_4$$

127 grams of iodine are here equivalent to 32 grams SO_2, to 63 grams Na_2SO_3 or to 126 grams $Na_2SO_37H_2O$.

61. *Determination of copper indirectly.*

When potassium iodide is added to a solution of copper sulphate the following reaction takes place,

$$\underset{\substack{2\times(63+32+64)\\2\times159}}{\underbrace{2CuSO_4}} + 4KI = \mathbf{Cu_2I_2} + \underset{2\times127}{I_2} + 2K_2SO_4$$

Every 63 parts of copper (or 159 parts of anhydrous copper sulphate) are equivalent to 127 parts of iodine.

The copper solution must not contain any free mineral acid. To ensure this being the case sodium carbonate is added to the solution until a faint permanent precipitate forms: acetic acid is then added carefully till the copper precipitate just dissolves. The free iodine is titrated with standard thiosulphate and starch and the copper calculated.

62. *Methods based on precipitation.*

In explaining the principles of volumetric analysis (***3*** and ***4***) the precipitation of silver chloride by the interaction of solutions of sodium chloride and silver nitrate was used as an illustration. Standard solutions of the latter salt can therefore be employed to determine the amount of halogen in any soluble chloride, provided an accurate way of determining the "end-point" is known. The reaction,

$$\underset{58.5}{\underbrace{\overset{}{\underset{23+35.5}{NaCl}}}} + \underset{170}{\underbrace{\underset{108+14+48}{AgNO_3}}} = \mathbf{AgCl} + NaNO_3$$

indicates that 170 grams silver nitrate are equivalent to 35.5 grams chlorine, 58.5 grams common salt, and so on for any other chloride that permits of this method being used. The completion or end-point of the reaction can be seen by agitating the precipitated silver chloride until it coagulates, and consequently settles, and then ascertaining whether or not an additional drop of either reagent will yield a milkiness or opalescence. But this method requires special precautions—one might almost say special apparatus—and in *neutral* solutions of chlorides it is easier to take advantage of the fact that when silver nitrate is added to a mixture containing a chloride and a small quantity of a chromate, *all the chlorine will be precipitated as* **AgCl** *before the chromate of silver* ($\mathbf{Ag_2CrO_4}$) *forms.* Chromate of silver has a chocolate-red colour and hence the first trace of an excess of silver salt, above that which is necessary to convert all the chlorine in the solution into white silver chloride, will be rendered apparent by the appearance of the permanent pink or orange tint that silver chromate imparts to the solution and suspended silver chloride. Silver chromate only serves as an indicator in *neutral* solutions, free acid preventing its formation. As chlorides in potable waters are estimated in this way solutions of fiftieth normal and even hundredth normal silver nitrate are often employed.

63. Determination of chlorine in a dilute solution of common salt.

A few drops of *yellow* potassium chromate ($K_2 Cr O_4$) are added to a known volume of the salt solution, the whole suitably diluted with distilled water and a standard solution of silver nitrate—say $\frac{N}{50}$ —run in, the contents of the vessel being stirred or shaken to ensure thorough mixing. As soon as a permanent reddish colour appears and remains in the turbid liquid after proper agitation, the preciptation of the chlorine as silver chloride is complete. As each c.c. of $\frac{N}{50} AgNO_3$ is equivalent to .00071 gram chlorine the amount of common salt present is readily ascertained.

In a similar manner the student should determine the strength of the laboratory ammonium chloride and of the calcium chloride. (Ca, 40).

64. Indirect estimations by means of standard silver nitrate.

As the completion of the reaction between silver nitrate and a soluble chloride is readily observed through the use of the chromate indicator it is evident that all compounds capable of being converted into neutral chlorides by evaporation to dryness with hydrochloric acid can be accurately determined in this way. The ***alkalies, alkaline-earths*** and many other bases can thus be estimated, as also ***chlorates*** and ***nitrates.*** The chlorine only is determined and the result calculated to the particular salt under examination. ***Chlorates*** are converted into chlorides by ignition and the chlorine then determined. ***Nitrates*** are evaporated on the water-bath with concentrated hydrochloric acid once or twice till the nitric acid is all expelled, heated in an air-bath to about 120°C, redissolved and titrated with standard silver solution.

65. Determination of sodium and potassium chlorides when mixed.

The total weight of the mixed chlorides of potassium and sodium is obtained by weighing, and the chlorine estimated by standard silver nitrate. If S represent the weight in grams of the sodium chloride and potassium chloride mixed, and C the weight in grams of the total chlorine found, then X, the number of grams of sodium chloride in the mixed chlorides, is found from the formula,

$$X = \left(2.10324 \times C - S\right) \times 3.6426.$$ (30)

The amount of potassium chloride will be (S – X) grams.

(30) This formula is obtained as follows:
Let X represent the number of grams sodium chloride in the mixed chlorides.
Let S represent the sum of the mixed chlorides.
Let C represent the total chlorine found.
Let Cl, NaCl, KCl, represent the reacting weights of chlorine, sodium chloride, and potassium chloride respectively, namely, 35.45, 58.5, and 74.56;
Then, as 1 NaCl requires for its formation 1 Cl,

X grams sodium chloride require $\frac{Cl}{NaCl} \times X$ grams chlorine,

and (S – X) grams potassium chloride require $\frac{Cl}{KCl}(S - X)$ grams chlorine.

$$\therefore \frac{Cl}{NaCl} X + \frac{Cl}{KCl}(S - X) = C$$

$$i.\,e.\ X\left(\frac{Cl}{NaCl} - \frac{Cl}{KCl}\right) = C - \frac{S \times Cl}{KCl}$$

Multiplying both sides of this equation by $\frac{KCl}{Cl}$ we get

$$X \times \frac{KCl}{Cl} \times \frac{Cl\,(KCl - NaCl)}{NaCl.\ KCl} = \frac{KCl}{Cl} \times C - \frac{S \times Cl}{KCl} \times \frac{KCl}{Cl}$$

$$i.e.\ X\left(\frac{KCl - NaCl}{NaCl}\right) = \frac{KCl}{Cl} \times C - S$$

$$X = \left(\frac{KCl}{Cl} \times C - S\right)\left(\frac{NaCl}{KCl - NaCl}\right)$$

The values of the above symbols are:— (using 35.45, 23.05, and 39.11 as the atomic weights of Cl, Na, and K, respectively). KCl=74.56, NaCl=58.50, $\frac{NaCl}{Cl} = 1.6502$, $\frac{KCl}{Cl} = 2.10324$, $\frac{NaCl}{KCl - NaCl} = 3.6426$; hence the formula given above.

66. Determination of the "available chlorine" in bleaching-powder.

Bleaching-powder is a compound of uncertain composition containing the chloride, hypochlorite and probably the hydrate of calcium, sometimes even the chlorate : if composed of the first two its composition would be $CaCl_2$ $Ca2ClO$; more often half this formula is taken, namely $CaOCl_2$, the "chloro-hypochlorite" of calcium. Were bleaching powder entirely $CaOCl_2$ then all the chlorine would be "available" for bleaching or oxidising purposes(31) ; but so many changes take place in its composition that in place of having 55% of its weight of chlorine available, as the formula $CaOCl_2$ would indicate, it seldom has more than 35% and sometimes as little as 20%. In valuing bleaching powder the object is to ascertain how much chlorine *capable of liberating oxygen from water* the sample contains. This is done in several ways, one of them being to determine its oxidising power on a solution of arsenious oxide, a reaction expressed by the equation,

$$\underset{198}{As_2O_3} + \underset{2(40+16+2\times 35.5)}{2CaOCl_2} = As_2O_5 + 2CaCl_2$$

Thus, 198 grams of arsenious oxide are equivalent to 4 × 35.5 grams of chlorine, and consequently to 2 × 16 grams of oxygen. Therefore $\frac{198}{4}$ grams arsenious oxide are equivalent to 35.5 grams chlorine and to 8 grams oxygen. A decinormal solution of this must contain $\frac{198}{40}$ grams, and each c.c. will be equivalent to .0035 gram Cl. The amount of chlorine found as the result of titrating a sample of bleaching-powder with arsenious oxide is known as the "available chlorine."

The indicator used to determine the end-point of the reaction is commonly called "starch-paper," but is more properly "starch-iodide-paper," for it consists of strips of bibulous paper that have been dipped in a mixture of starch solution and potassium iodide—about one part of starch and of the iodide to a hundred parts of water—and allowed to dry. Any substance capable of liberating iodine from potassium iodide will cause this starch-paper to turn blue and the presence of any unacted-on bleaching-powder in the solution being examined will at once be observed if a drop of it is brought in contact with the test-paper. The titration is done as follows.

67. A known volume of the bleaching-powder solution(32) is placed in a flask, diluted somewhat with water and the standard solution of arsenic(33) run into it from a burette. From time to time a drop of the solution is removed on the end of a glass stirring-rod and brought into contact with a strip of the starch-paper. As soon as no colouration is produced on the paper the reaction is complete and the volume of arsenic solution is noted. Two more determinations should be done in a similar manner to ensure an accurate result, for the frequent removal of drops in the process of "spotting" the starch-paper will of necessity lessen, though slightly, the total volume of solution subjected to the action of the arsenic solution.(34) From the quantity of arsenic solution required the amount of "available chlorine" per litre of the bleaching-powder solution is calculated.

68. Determination of "available chlorine" by iodine and thiosulphate.

If hydrochloric acid be added to a solution of bleaching powder *containing some potassium iodide*, the chlorine liberated by the action of the acid on the bleaching compound will in turn liberate an equivalent amount of iodine from the potassium iodide. This quantity is readily determined by titration with sodium thiosulphate and starch, ***51***. 127 grams of iodine being equivalent to 35.5 grams of chlorine, the "available chlorine" in the sample is easily found.

Take 20 c.c., or any other known volume, of the solution of bleaching-powder (note 32), add an excess of potassium iodide solution and enough dilute hydrochloric acid to render the liquid decidedly acid. Then titrate the liberated iodine with starch and thiosulphate and from this calculate the amount of available chlorine.

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(31) That is, for liberating nascent oxygen from water, the oxidising power of chlorine being dependent on the presence of water,—$Cl_2+H_2O=2HCl+O$. This would also be the amount of chlorine available for "chlorinating" purposes.

(32) Bleaching-powder, as will be readily seen from what has been said regarding its composition, is not completely soluble in water. A solution of it is best prepared by triturating a weighed sample with water in a mortar, allowing it to settle and pouring the clear liquid into a litre flask. This process is repeated once or twice and the whole of the powder, whether in solution or not, finally washed into the flask, which is filled up to the mark. Before the withdrawal of a sample for analysis the flask and contents must be shaken. The solution, which is always slightly milky, deteriorates rapidly.

(33) To prepare a decinormal solution of arsenious oxide, $\frac{198}{40}$, *i.e.*, 4.95 grams of the pure resublimed oxide are placed in a litre flask with about 250 c.c. of distilled water and about 20 grams of pure sodium carbonate. After heating on a water-bath and shaking, the arsenious oxide dissolves : the flask is then cooled to room temperature and the contents made up to a litre.

(34) See last paragraph of ***44***.

69. Determination of nitrogen.

Perhaps the most rapid, simple and at the same time accurate method for determining nitrogen is that first proposed by Kjeldahl and which bears his name. Other chemists (notably Gunning, Wilfarth and Jodlbauer) have improved on the original method and made it applicable to the determination of nitrogen in innumerable organic and inorganic compounds. Coal, grain, fertilisers, nitrates, ferro- and ferricyanides, nitro-compounds, azo-compounds, indigo, nitriles, urea, and bodies of almost every class will, when suitably treated by this method, yield up their nitrogen in the form of ammonia, which is then determined volumetrically. Broadly speaking, the process consists in heating the substance with concentrated sulphuric acid which abstracts the elements of water, oxidises the carbon and is itself reduced to sulphur dioxide. This acts as a reducing agent on the nitrogenous matter, yielding, with the sulphuric acid present, ammonium sulphate. The ammonia is then liberated from the salt by boiling with caustic alkali, distilling it off into an excess of (a known volume of) standard acid, and determining the amount of acid which it neutralises by titration with standard alkali: from this the amount of nitrogen is found. The higher the temperature at which the sulphuric acid acts the easier will the oxidation take place and the process thereby be shortened. It is usual, therefore, to add powdered potassium sulphate to the sulphuric acid after the latter has acted on the material for some time and all frothing is over, thus obtaining a strongly acid solution of potassium hydrogen sulphate whose boiling point is much above that of the sulphuric acid itself. The addition of a globule of mercury, or a little precipitated mercuric oxide, is recommended by some, to render the process still more rapid, but, if this is used, a subsequent addition of sodium or potassium sulphide is necessary, prior to distillation, to decompose any mercurammonium compounds that may be formed. When natural organic products are being analysed an excess of sulphuric acid should be employed.

The effect of the sulphuric acid is, as is explained above, to break up the body completely, in some cases very readily and in others after long continued boiling; but the complete conversion of the nitrogen present as nitrates ("nitric" nitrogen) into ammonia ("organic" nitrogen) is not effected by the action of boiling sulphuric acid alone. Four cases therefore present themselves:

(*a*) *The determination of total nitrogen when there are no nitrates present.* The substance is treated as described in the sequel (***70***).

(*b*) *The determination of total nitrogen when there are nitrates present.* A slight modification of the first method serves to ensure the total nitrogen present in the substance being obtained in the form of ammonia. Salicylic acid or phenol is added to the sulphuric acid used for oxidation, preferably the former, in the proportion of about 40 grams to a litre of concentrated sulphuric acid, of which mixture 30 c.c. is a suitable amount to employ with about 1 gram of the nitrogenous substance. The process of reducing the nitrates is facilitated by the addition of 2 or 3 grams of zinc dust and a drop of mercury. Sodium thiosulphate has a similar effect. The action if the salicylic acid is to yield with the nitric acid of the nitrate a nitro compound, this being reduced to an amido compound which in the subsequent treatment with caustic alkali gives up its nitrogen in the form of ammonia.

(*c*) *Determination of "organic" nitrogen, including that present as ammonia, in the presence of "nitric" nitrogen.* To determine the former only, it is necessary that all nitric nitrogen should be removed from the solution. This can be done by heating the weighed substance containing nitrates with ferrous sulphate and concentrated hydrochloric acid, thus expelling all nitric acid. The residue is heated and the nitrogen determined as in ***70***. Another method of getting rid of the nitrates is to add to the sample concentrated sulphuric acid containing formic acid in the proportion of 10 c.c. of the latter (of s.g. 1.22) to 5 c.c. of the former. The formic acid is oxidised by the liberated nitric acid, first to oxalic acid and finally to carbon dioxide and water, the nitric acid becoming nitric oxide which is driven off on heating. The nitrogen can then be determined as in ***70***.

(*d*) *Determination of ammonia in free ammoniacal compounds, when nitrogenous organic matter is also present.* Schlösing's method should be employed for this. For detailed instructions see *Fresenius, sixth edition, Vol.* 1, § 99, *b*.

70. Determination of nitrogen in the absence of nitrates.

Introduce a weighed quantity of the substance (35) into a round-bottomed pear-shaped flask of hard Jena glass (special flasks with necks from six to ten inches long are made for this purpose) of about 500 c.c. capacity (36) and add a drop of mercury, or about .5 gram of precipitated mercuric oxide. 20 or 30 c.c. of concentrated sulphuric acid (free from nitrogen) (37) is poured in, the contents of the flask rotated to ensure thorough mixing, and heated in the fume cupboard, gently at first, gradually raising the temperature till the liquid boils briskly. After 10 or 15 minutes boiling the flame is removed, about 10 grams of dry powdered potassium or sodium sulphate added and the heating continued till the contents of the flask are clear and practically colourless. The flask should be inclined on one side and a loosely fitting stopper having a long end projecting inwards, or a small filter-funnel, inserted in its neck to obviate any loss through spirting.

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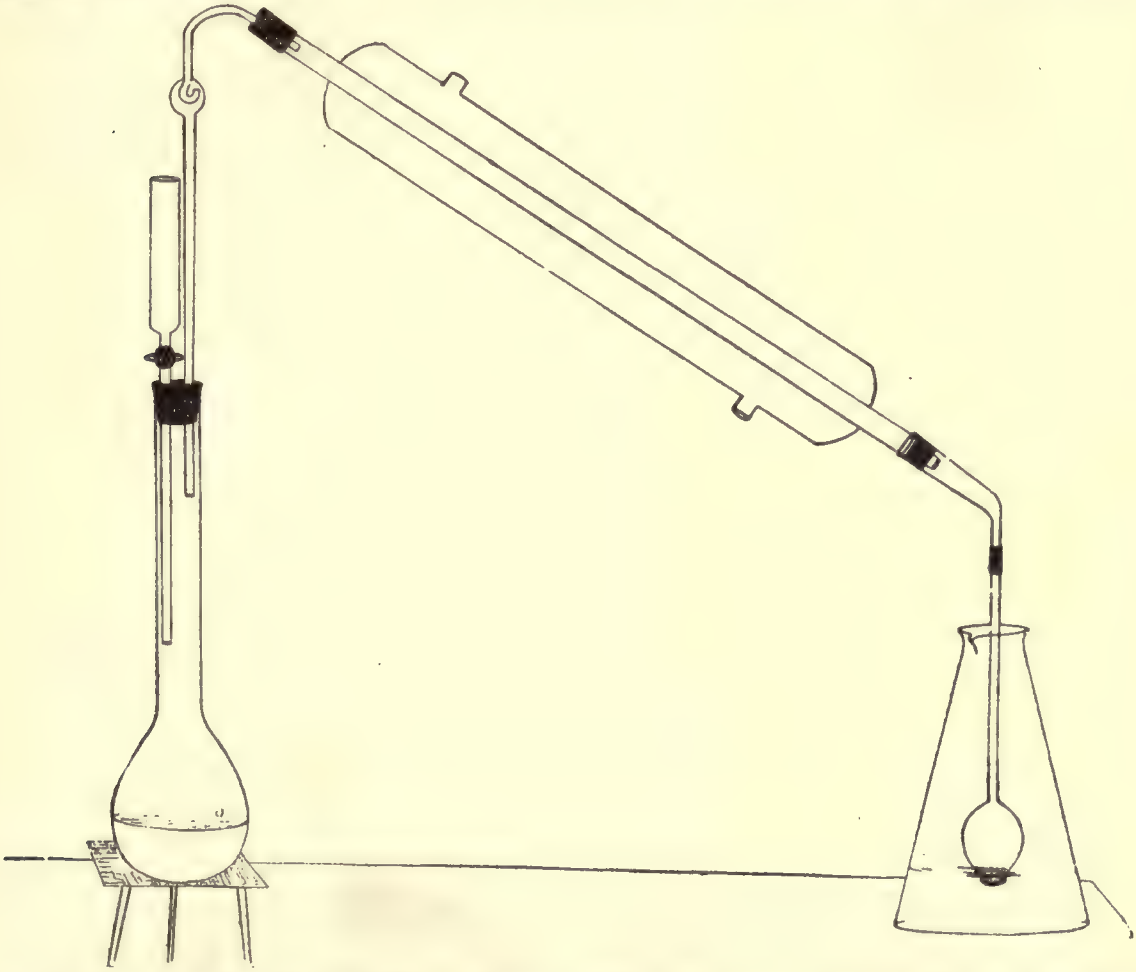
(35) The amount will vary according to the nature of the substance, from .2 gram to 5 grams may be used. About .5 gram of urea or of acetanilid does very well for practice.

(36) The use of a large flask renders unnecessary the subsequent transference of the solution to a distilling-flask.

When the reaction is complete allow the flask and contents to cool, cautiously dilute the solution with about 250 c.c. of distilled water (ammonia-free) and drop in one or two pieces of granulated zinc or of broken pumice to prevent "bumping." At once attach the flask by means of a two-holed rubber stopper to a condensing apparatus such as that shewn in the figure. Through the tap-funnel in the second hole is introduced enough of a saturated solution of sodium or potassium hydroxide (free from nitrogen) to render the strongly acid mixture alkaline, following it with sufficient potassium sulphide solution (containg about 40 grams to the litre) to precipitate all the mercury or mercuric oxide, if that was previously added. Heat and distil off the ammonia into a measured quantity of decinormal sulphuric acid. (38) The excess of standard acid is then titrated as described in ***29*** with standard alkali of the same strength and the percentage of nitrogen in the sample calculated from the amount of ammonia found.

The figure illustrates how the distillation apparatus may be fitted up. (39) A block-tin condensing tube is better than a glass one, as the latter is acted upon to a slight extent by steam, yielding traces of alkali.



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(37) All reagents must be carefully tested by blank experiments. About half a gram of pure cane sugar should be treated with the same quantities of sulphuric acid and other reagents that are to be used in the process and the amount of ammonia thus found taken into account in calculating the result of the determination.

(38) The first 150 c.c. of the distillate will contain practically all the ammonia, but the next portion, nevertheless, should be received in a beaker containing a little water and a drop of the indicator to be used in the titration. If there is any sign of its being alkaline, what is collected must be added to the first distillate and this repeated till no trace of alkalinity can be detected.

(39) Most laboratories possess a heating and distilling apparatus for performing several nitrogen determinations at the same time. Illustrations of these can be found in any dealer's catalogue.

The use of the tap-funnel for the admission of the caustic alkali is not essential: it may be added directly to the solution, but then there is a danger of some ammonia being lost before the flask can be attached to the condensing tube.

As alkali is apt to be mechanically carried over with the distillate, the tube should rise some twelve or eighteen inches before being bent over. Numerous forms of "traps," also, are made use of for this purpose. The adapter delivering the ammonia and water into the standard acid should be made pear-shaped (an inverted funnel works well, also) and should be immersed only a small distance under the surface of the acid: variations of pressure during distillation will then cause no "running back."

71. Determination of total nitrogen when nitrates are present.

Make up the solution of salicylic acid in concentrated sulphuric acid that is described in **69,** *b*, and pour quickly about 30 c.c. of this on to the substance whose total nitrogen it is desired to estimate: the rapid addition of the acid prevents the liberation of lower oxides of nitrogen, which would occur were the substance not completely covered by the salicylic-sulphuric acid mixture immediately.(40) Shake and add to the contents of the Kjeldahl flask, while still cold, 2 or 3 grams of zinc dust and about a gram of mercury and allow these to dissolve slowly before heating. Continue the determination from this point exactly as described in **70.**

(40) *Trans. Chem. Soc.*, LXVII., 1895, 814.

GRAVIMETRIC ANALYSIS

72. A short explanation of the principles underlying analyses done by gravimetric methods is given in **1**. The element or acid radicle is converted into some compound of known and constant composition—in some cases the element itself—which is then weighed. In the operations of solution, precipitation, washing, drying, ignition and final weighing, a substance is inevitably subjected to so many processes that some instructions as to manipulation are necessary at this stage, though an ounce of demonstration in the laboratory is worth many pounds of written directions; very little space, therefore, will be taken up in this way and what guidance is given here will require to be largely supplemented by the instructor.

73. *Solution and Evaporation.*

In preparing a solid for examination great care must be taken that none of it is lost in transference to the beaker or flask in which its solution is to be effected. If weighed on a watch-glass every trace of it must be washed into the flask by means of a *fine* jet of water from a wash-bottle. The student will find the work greatly facilitated by having a supply of hot water always in the wash-bottle, protecting the hands by a piece of towelling wound round and secured to its neck. The flask or beaker should be placed on wire gauze or on a sand-bath over a bunsen burner and possible loss of material through "spurting" in the course of heating to effect complete solution is best avoided by covering the beaker with a large watch-glass or, in the case of an Erlenmeyer (or other form of) flask, by inserting a filter funnel in its neck. All moisture or material that collects on the watch-glass or funnel is carefully rinsed into the flask with water from the wash-bottle after solution is complete. In heating on the sand-bath do not use too much sand in it; a thin layer is all that is required to ensure the uniform heating of the vessel placed on it. The level of the liquid in a beaker or flask must not be allowed to become too low or there is danger of cracking. In evaporating solutions in a porcelain basin drops are liable to be ejected on heating; this may be avoided by placing an inverted filter funnel of suitable size over it, the edge of the funnel resting on the walls of the basin above the level of its contents. Liquids often have a tendency to creep up the sides of the vessels in which they are boiled or evaporated and care must be taken to remove the crust that is formed in this way, as well as any liquid or solid matter that may adhere to the inverted funnel, along with its contents.

74. *Precipitation*, to convert a substance in solution into an insoluble one, is best done in a beaker having a lip and in *hot* solutions. After the addition of the precipitant the precipitate is well stirred and allowed to settle; a few more drops of the reagent are added to the clear liquid to make sure that precipitation is complete, but a large excess must be avoided. By stirring and boiling, precipitates assume a granular condition, settle more rapidly and are more easily filtered. *Hot solutions pass through a filter much quicker than cold ones.*

75. *Filtration and washing precipitates.* The beaker containing the precipitate and liquid is allowed to stand till the precipitate has settled, when the clear liquid is decanted cautiously on to the filter, previously wetted, by pouring it down a glass rod held against the edge of the lip, care being taken to disturb the precipitate as little as possible. The filter must not be filled too full; drops are prevented from finding their way down the outside of the beaker by a proper use of the glass rod. After most of the liquid has been decanted through the filter, hot water is added to the contents of the beaker which are stirred and heated to boiling once more. After settling, the liquid is again poured through the filter and the operation repeated two or three times: this is known as "washing by decantation." Finally the precipitate is transferred to the filter by means of a fine jet of water from the wash-bottle. Some of the precipitate is apt to adhere to the walls of the beaker and this can be removed by playing on it a stream of water from the wash-bottle and, at the same time, rubbing it off with a glass rod tipped with about half an inch of narrow rubber tubing: a rod thus armed is known as a "policeman." The final washing of the precipitate is done on the filter. Filtration is facilitated and losses through splashing are avoided by letting the end of the funnel rest against the edge of the vessel that is receiving the filtrate. The liquid and precipitate must never completely fill the filter-paper—the latter never more than half—and each lot of wash-water must be allowed to drain through before more is added. The final wash-water, as it runs through, is tested to see that it is free from all soluble matter, otherwise this would add to the weight of the precipitate and would also render inaccurate any subsequent determination in the filtrate.

76. Drying precipitates. From what has been said in **1** it will be seen that, in the majority of cases, precipitates after washing are dried, ignited and weighed until the weight is constant. The drying process takes considerable time but there are occasions when it may be dispensed with and the filter-paper and its contents directly ignited. When drying-ovens are available in which to place the precipitate and funnel it is best to cover the latter with a piece of moist filter-paper on which may be previously written, as a safeguard against possible mistakes, the nature of the precipitate contained in it. A quicker method is to suspend the funnel over the chimney of an argand burner. Another way is to remove the filter-paper and its contents carefully from the funnel and to lay it on its side (with an intervening sheet of paper) on a piece of glass placed on the upper part of a "hot-plate," easily made by bending a piece of sheet iron into the form of a rectangular parallelopiped, (like a shallow box lacking the ends). The lower side of this is heated gently by a bunsen burner, the air space between the iron surfaces preventing the paper being subjected to too high a temperature.

77. Ignition of precipitates. When dry, the precipitate is transferred to a weighed porcelain (or platinum) crucible—previously heated to redness and cooled before weighing—and the paper, with what of the precipitate adheres firmly to it, rolled up loosely and secured by taking a turn round it with a platinum wire fixed in a glass rod. The paper is held over the crucible and there burned, the remains of the precipitate and the ash of the paper being allowed to fall into it. The crucible is then placed on a pipeclay triangle and heated with a direct flame till all the unconsumed carbon of the paper is burned away; after being heated strongly for a few minutes it is cooled and weighed. In some cases the carbon of the paper exercises a reducing action on the precipitate: removing the precipitate as completely as possible from the paper as described minimises this action very considerably, but *if any reduction takes place the precipitate will not be uniform in composition and therefore wholly unsuitable for weighing.* As such cases occur in the examples that follow, instructions for dealing with them will be given.

TYPICAL EXAMPLES OF GRAVIMETRIC ESTIMATIONS

78. Determination of iron.

Ferrous-ammonium-sulphate, ($FeSO_4$, $(NH_4)_2SO_4$, $6H_2O$), known as Mohr's salt, may be used for this estimation: before precipitation it requires to be oxidised to the ferric salt and afterwards converted into ferric hydroxide by the addition of ammonia.

Weigh out about a gram of the salt on a watch-glass and transfer it completely to a beaker; cover with hot water to the depth of an inch or so and warm, adding a little concentrated nitric acid to oxidise the iron. A brown colouration will be produced owing to the reduction of the nitric acid and the absorption of the nitric oxide by the ferrous salt. Heating is continued until the addition of a drop of nitric acid causes no further change. The complete oxidation of the iron to ferric salt may be confirmed by using a solution of potassium ferricyanide as an outside indicator in the manner described under ***44***.

To the hot solution is added ammonia in excess, that is, till the solution smells strongly of this reagent, the mixture stirred with a glass rod armed with a rubber tip (***75***) and boiled till the greater portion of the ammonia is expelled. After the precipitate has settled, the hot liquid is cautiously decanted through a filter, the precipitate washed once or twice by decantation (***72***) and finally transferred to the filter where it is subjected still further to the washing process until the washings contain no trace of soluble matter.(41) In washing the precipitate on the filter it should be collected as far as is possible in a compact mass in the cone of the filter leaving the upper edges of the paper perfectly clean. After allowing it to drain for a few minutes, the filter with the precipitate is carefully removed from the funnel and laid on its side on a piece of paper resting on the hot-plate, where it is dried. While the precipitate is drying, a porcelain (or platinum) crucible, resting on a pipeclay-triangle over a bunsen burner, is heated to redness, cooled,(42) weighed and placed on a piece of glazed paper on the table in readiness to receive the precipitate.

When dry, the precipitate is loosened by gently squeezing the filter paper and as much of it as possible transferred to the crucible, the paper being treated as described in ***77***. Any particles of ash or precipitate that have fallen outside the crucible can readily be gathered together on the glazed paper by means of a camel's hair brush or feather and added to the contents of the crucible which is then heated to redness for about ten minutes, cooled and weighed.(43)

From this the quantity of iron is calculated as follows:

Weight of watch-glass .... grams.
Weight of watch-glass + salt.......................... grams.

Weight of salt taken................................ grams.

(Here the student should enter a concise description of the operations carried out.)

Weight of crucible + Fe_2O_3 + ash........................ grams.
Weight of crucible.................................... grams.

Weight of Fe_2O_3 + ash .... grams.
Deduct weight of ash .... grams.

Weight of Fe_2O_3 .... grams.

Calculating this to iron,

$$\underbrace{Fe_2O_3}_{160} : \underbrace{Fe_2}_{112} = \text{Wt. of } Fe_2O_3 \text{ found} : x \text{ grams iron in sample.}$$

$$x = \text{Wt. of } Fe_2O_3 \text{ found} \times \frac{112}{160} \text{ grams.}^{(44)}$$

$$\text{Therefore, the percentage of iron} = x \times \frac{100}{\text{Wt. of sample}}$$

The student should compare this result with the theoretical percentage of the element in the salt used for analysis. Mohr's salt being $FeSO_4$, $(NH_4)_2SO_4$, $6H_2O$, molecular weight 392, the percentage of iron in it, x, is found from the proportion,

$$392 : 100 = 56 : x$$

$$\therefore x = \frac{56 \times 100}{392} = 14.28$$

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(41) The soluble matter in contact with the precipitated Fe $(OH)_3$ in this case is ammonium sulphate, and may be tested for by collecting a few c.c. of the washings in a test tube and adding $BaCl_2$ which will cause a milkiness, due to $BaSO_4$, as long as there is any salt present.

(42) Where one is available, a desiccator should be used in which to cool crucibles and to carry them backwards and forwards between the balance and the table.

(43) Any Fe_2O_3 that may be reduced by the paper to metallic iron is reconverted into oxide on ignition.

(44) See ***2***. The fraction $\frac{112}{160}$ is the "factor" for calculating Fe_2O_3 to Fe. Many books supply these factors, with little or no explanation of how they are obtained.

79. Determination of aluminium.

The process described in **78** is applicable to the estimation of aluminium (and of chromium); ordinary potash-alum may be used for the experiment.

From 1 to 2 grams of alum ($KAl2SO_412H_2O$) are weighed out, placed in a beaker, dissolved in hot water, ammonium chloride added, (45) the solution heated to boiling and the aluminium precipitated as hydroxide by the addition of a slight excess of ammonia. The washing and filtering processes are the same as described in **78**. In this case, however, drying of precipitate and filter *may* be dispensed with and the wet filter and its contents cautiously ignited in a crucible covered with a lid that should not be removed until all moisture and gases have been expelled. The heating must be very gradual, quite a small flame being used at some distance below the crucible and the heat slowly increased as incineration begins. The precipitate is weighed as Al_2O_3. The result is calculated as in **78**. (Al, 27).

80. Determination of chromium.

Use chrome-alum ($KCr2SO_412H_2O$) and follow the instructions laid down in **78** and **79**. The addition of ammonium chloride—necessary in the case of the aluminium—may be dispensed with in precipitating chromium. (Cr, 52).

81. Determination of copper by weighing as oxide.

Non volatile organic substances, such as tartaric acid and sugar, and also alkaline nitrates, prevent the complete precipitation of copper as hydroxide, (as also of the hydroxide of other metals).

Weigh out about a gram of pure recrystallised copper sulphate ($CuSO_45H_2O$) into a beaker, dissolve it in about 100 c.c. of water and heat to boiling. Then add potassium or sodium hydroxide in small quantities at a time, constantly stirring the solution till precipitation is complete and a *slight* excess of alkaline hydroxide is present. This will be the case when the liquid—after boiling and the precipitate allowed to settle—is colourless and yields an alkaline reaction with test-paper. The contents of the beaker are again boiled, when the copper hydroxide loses water and becomes black copper oxide. Let the precipitate settle, decant the clear liquid through a filter, wash once or twice by decantation and transfer the precipitate to the filter, washing it until the washings, on being tested, are free from soluble matter (*See note* (41)). Dry the paper and precipitate, remove the latter from the paper as completely as possible to a weighed porcelain crucible, burn the paper, add the ash,—letting it fall on a part of the crucible where there is no precipitate,(46)—and ignite till all carbon is burned off.

As contact with the hot carbon of the paper will have converted some of the easily reduced copper oxide into metallic copper, a drop of concentrated nitric acid is added which converts any free copper into copper nitrate. Heat is now applied gently, the free nitric acid is thus expelled, the copper nitrate becomes copper oxide, and the final heating of the crucible to redness for about ten minutes ensures its contents being entirely **CuO**. In this form it is weighed and the percentage of copper present in the crystallised sulphate calculated. (Cu, 63).

The theoretical percentage of copper in $CuSO_45H_2O$ is 25.35.

82. Determination of sulphuric acid ($''SO_4$), in a soluble sulphate.

The sulphuric acid radicle is converted into insoluble barium sulphate (**$BaSO_4$**), by precipitation with barium chloride, and weighed as such. This method has a wide application; the sulphur content of any body can, by suitable treatment, be converted into sulphuric acid or a soluble sulphate, and this, in turn, into barium sulphate: from the weight of this precipitate the amount of sulphur is found and calculated to the form in which it originally existed in the substance being analysed.(47)

Weigh out from .5 gram to 1 gram of potassium-alum ($KAl2SO_412H_2O$),(48) into a beaker and dissolve it in water; acidify with a little hydrochloric acid, add some ammonium chloride solution,(49) heat to boiling and run in—in a very thin stream, shaking and stirring the while—a *hot* solution of barium chloride. Allow to partly settle and test the clear layer with a few more drops of barium chloride till complete precipitation is effected. Wash the precipitate two or three times by decantation, pouring the filtrate and washings through the filter and finally transfer it to the filter. Wash it further with hot water till the washings shew no trace of barium chloride when tested with silver nitrate, and, as directed in previous examples, let the final washing be devoted to collecting the precipitate in a compact mass in the apex of the filter.(50) The filter with the precipitate is then removed to the hot-plate and dried.

(45) $Al(OH)_3$ is only *completely* precipitated by ammonia when ammonium chloride is present.

(46) If the crucible containing the CuO is tapped on the table gently, the precipitate will collect on one side, leaving a clear space for the ash. The platinum wire holding the paper should be wound round that part of it which is away from the portion to which the precipitate is adhering.

(47) The presence of large amounts of nitric acid, nitrates and chlorates interferes with the precipitation of $BaSO_4$, as also does an excess of hydrochloric acid. Barium and strontium are also estimated as sulphates. The latter requires a considerable volume of alcohol added to the aqueous solution to ensure complete precipitation.

(48) Alum is chosen here as it admits of accurate weighing, being unaffected by atmospheric conditions. Any other soluble sulphate may be used, however.

(49) Ammonium chloride causes the $BaSO_4$ to precipitate in a more granular form than it otherwise would. It is often a troublesome precipitate to filter, having a tendency to pass through the paper. Precipitation in hot solutions may prevent this but more often long continued boiling must be resorted to or special filter-papers employed.

(50) In the determination of barium (and of strontium), the precipitant is dilute sulphuric acid and very thorough washing is required before this is wholly eliminated. The washings must be *absolutely free from acid before drying*, otherwise the paper will char or become so brittle that handling it in the subsequent burning process becomes almost impossible.

The precipitate, after drying, is detached from the paper as completely as possible and removed to a weighed crucible—the lid being weighed along with it, as it will be found advisable to cover the crucible at a later stage in the process of ignition. The paper is burned and the ash, with the adhering barium sulphate, allowed to fall into the crucible, preferably on another part than that on which the precipitate is resting (*note* 46). The crucible is then heated to redness till all carbon particles are consumed and allowed to cool. Any barium sulphate in contact with the paper will have been reduced to barium sulphide (**BaS**) during incineration and must be reconverted into **$BaSO_4$**. To do this, moisten the ash with one or two drops of dilute hydrochloric acid, add a drop or two of dilute sulphuric acid, cover the crucible with the lid to prevent loss by spirting and apply a gentle heat until the acids and moisture are expelled; heat to redness for about ten minutes, then cool and weigh. From the weight of **$BaSO_4$** the percentage of ″SO_4 may be calculated.

83. *Determination of lead as sulphate ($PbSO_4$).*

To a weighed quantity of lead nitrate or acetate,(51) dissolved in water, add dilute sulphuric acid in moderate excess(52) and, to render precipitation complete, about twice as much alcohol (methylated spirit will do) as there is solution. Stir well, allow the precipitate to settle, filter and wash on the filter with alcohol till the washings are free from any trace of acid (*note* 50). After drying, separate the precipitate as completely as possible from the paper and transfer it to a perfectly dry watch-glass. Burn the paper (with the adhering lead sulphate) in a weighed porcelain crucible and to the resulting metallic lead—produced by the reduction of the lead sulphate during the incineration process—add a few drops of nitric acid which will form with it lead nitrate. To this add two drops of concentrated sulphuric acid, heat cautiously at first to expel the acids and, when quite dry, add the precipitate from the watch-glass and ignite at a dull red heat for ten minutes. Cool and weigh. Repeat the heating and weighing until the weight is constant and from the result calculate the percentage of lead. (Pb, 207).

Another way of treating this precipitate is to remove it from the paper to a weighed porcelain crucible and to burn the paper in an inverted crucible-lid. The residue left after all the carbon of the paper has been burned off and the lid allowed to cool, is moistened with a few drops of nitric acid, sulphuric acid added as before and the acids cautiously expelled by heat. Crucible and lid are then heated together, cooled and weighed.

84. *Determination of magnesium.*

Magnesium sulphate ($MgSO_47H_2O$) may be used for this estimation. The magnesium is precipitated as **$MgNH_4PO_46H_2O$**, a crystalline precipitate, by the addition of sodium phosphate (Na_2HPO_4) to solutions of magnesium salts containing ammonium chloride and ammonia. The reaction may be represented thus,

$$MgSO_4 + NH_4HO + Na_2HPO_4 = \mathbf{MgNH_4PO_4} + Na_2SO_4 + H_2O$$

Ammonia in excess of that required by this equation must be present, as the double phosphate is slightly soluble in water but insoluble in the presence of free ammonia. If ammonium chloride is not added first, the ammonia will precipitate the magnesium as hydroxide (**$Mg(OH)_2$**); sufficient ammonium chloride must therefore be present to prevent this occurring.(53) The precipitate on ignition becomes the pyrophosphate (**$Mg_2P_2O_7$**) in which form it is weighed, and from this the magnesium calculated. (Mg, 24).

Dissolve about 1 gram of magnesium sulphate in water in a beaker and add to the solution ammonium chloride followed by ammonia in slight excess: the solution must remain clear after the addition of ammonia and will do so if there is enough ammonium chloride present. To the cold, clear solution add sodium (or ammonium) phosphate in excess and stir well, but *avoid contact with the walls of the beaker* which, if touched, will become coated firmly with the precipitate as it forms, and which is removeable only with extreme difficulty.(54) Cover the beaker and allow it to stand for at least six hours.(55) Filter and wash the precipitate with a cold solution of ammonia (1 part concentrated ammonia to 3 parts of water) till the washings shew no trace of soluble matter, but no longer. Dry the filter, separate the precipitate as thoroughly as possible from it (***83***), place the filter in a weighed crucible, moisten it with two drops of concentrated nitric acid and cautiously ignite. Cool, add the precipitate to the ash, ignite once more with a bunsen flame and finish off the ignition with the blow-pipe. Cool and weigh. Heat again till weight is constant.

(51) A little free nitric acid or acetic acid, according as the former or latter salt is employed, may be added to assist in clearing the solution. Use about 1 gram and about 150 c.c. of water only, as precipitation occurs all the more easily if the solution is concentrated.

(52) $PbSO_4$ is less soluble in dilute sulphuric acid than in water, hence the use of a moderate excess of acid.

(53) Magnesium hydroxide and ammonium chloride yield a soluble double salt, $MgCl_22NH_4Cl$. The behaviour of a soluble salt of magnesium with ammonia and the effect of ammonium chloride on the precipitate thus produced, are seen from the equations,

$$(a)\ 2MgCl_2 + 2NH_4HO = \mathbf{Mg(OH)_2} + MgCl_22NH_4Cl$$

$$(b)\ \mathbf{Mg(OH)_2} + 4NH_4Cl = 2NH_4HO + MgCl_22NH_4Cl$$

(54) Any precipitate that persistently adheres to the walls of the beaker must be dissolved off with hydrochloric acid and reprecipitated.

(55) The most convenient and time-saving procedure is to arrange that this precipitation takes place over night.

85. Determination of calcium.

The calcium in a soluble salt is usually estimated by precipitation as oxalate in the presence of ammonia. The precipitate may be collected on a tared filter, dried at 100° and weighed as CaC_2O_4,H_2O. It is more usual, however, to ignite the precipitated oxalate and weigh as carbonate, or to strongly heat it till conversion into oxide is complete and weigh it in that form. An accurate and quicker method is to determine the precipitated calcium oxalate volumetrically by titration with potassium permanganate, ***(41).***

To a hot solution of a calcium salt (best obtained by dissolving about 1 gram of calcium carbonate in the minimum of hydrochloric acid, keeping the vessel covered during the process of solution with a clock-glass to prevent loss by effervescence) add enough ammonia to impart to it a strong ammoniacal smell and then a slight excess of a boiling solution of ammonium oxalate ($(NH_4)_2C_2O_4$). Set the beaker aside in a warm place and allow it to stand over night. Test the supernatant liquid with a little more ammonium oxalate to make sure that precipitation is complete; filter, wash with hot water containing a little ammonia—by decantation first and finally on the filter. (56) Take care that every particle of precipitate is transferred to the paper as it tends to adhere to the glass and requires persistent rubbing with a policeman to ensure its removal.(57) The precipitated calcium oxalate may now be treated in different ways.

a. Weighing as carbonate (**$CaCO_3$**). Dry the filter and remove the precipitate as completely as possible from it to a weighed crucible. Burn the paper, letting the ash fall into an inverted crucible lid (also weighed) resting on the crucible. Heat very gently at first, (58) increasing the temperature gradually till the bottom of the crucible is faintly red, keeping it that way for about 20 minutes. Cool and weigh. As some $CaCO_3$ may have been converted into CaO and the composition of the precipitate, therefore, not constant, moisten the precipitate in the crucible and add a little solid ammonium carbonate. Evaporate cautiously to dryness, heat once more and weigh again. This must be repeated until the weight is constant.

b. Weighing as oxide (**CaO**). This is more expeditious and requires less patience than *a.* Place the filter-paper, without drying, in a crucible and heat—cautiously at first—to drive off the water and to incinerate the paper. When the carbon is all burned off, cover the crucible and ignite strongly for 10 or 15 minutes over the blow-pipe. Cool and weigh, repeating the heating and weighing until the weight is constant. (59)

c. Volumetric determination. Dissolve the precipitated calcium oxalate from the paper with dilute sulphuric acid and titrate the resulting oxalic acid with standard potassium permanganate as described in ***39***, ***40*** and ***41.***

From the result of any of these three methods the calcium can be calculated. (Ca, 40).

86. Estimation of phosphoric acid in a soluble phosphate.

Phosphoric acid, ($'''PO_4$), is precipitated as **$MgNH_4PO_46H_2O$**, ignited and weighed as **$Mg_2P_2O_7$**. It will be seen that this is the converse of ***84:*** the principle is the same but a soluble magnesium salt is the precipitatant. From the weight of the pyrophosphate the desired calculation can be made. (P, 31).

Dissolve about 1 gram of crystallised sodium hydrogen phosphate ($Na_2HPO_4,12H_2O$), in a beaker with about 100 c.c. of water. Make the solution faintly alkaline with ammonia, add a slight excess of magnesia mixture (60) and stir till the precipitate of magnesium ammonium phosphate has begun to form. Cover and set aside for at least 6 hours and treat the precipitate as described in ***84.***(61)

87. Determination of cupric and ferrous sulphates when mixed.

The copper is first completely separated from the iron by means of hydrogen sulphide which precipitates it as **CuS**, the copper sulphide is next converted into the oxide **CuO**, in which form it is weighed. In the filtrate from the copper precipitate the iron is estimated volumetrically by titration with $\frac{N}{10}$ permanganate of potassium. In a fresh portion of the sample the $''SO_4$ is precipitated and weighed as barium sulphate.

(56) In complex analysis the calcium oxalate precipitate always carries down with it traces of magnesium if the latter is present. To overcome this difficulty, dissolve the precipitate from the paper into a beaker with dilute hydrochloric acid; wash the paper thoroughly with hot water, heat the resulting solution to boiling and add dilute ammonium oxalate and ammonia in slight excess. Stir well and allow to settle, standing the beaker in a warm place as before; filter and wash the precipitate with hot water containing a little ammonia. The precipitate should be free from all traces of magnesium.

(57) If rubbing fails to remove it, the precipitate must be dissolved in a few drops of very dilute hydrochloric acid. ammonia added and the precipitate formed added to the first precipitate.

(58) If heated suddenly, the oxalate decomposes with separation of carbon. Heated slowly, the gradual separation of carbon and the transition of the precipitate from white to gray and finally to white again will be noticed.

(59) A useful check on this method is to add to the calcium oxide 2 or 3 c.c. of dilute sulphuric acid and ignite cautiously, repeating the process once or twice till the weight of the resulting calcium sulphate is constant.

(60) "Magnesia mixture." Dissolve 68 grams of magnesium chloride and 165 grams of ammonium chloride in water. Add 260 c.c. of ammonia solution and make up to 1 litre. 10 c.c. of this is about equivalent to ·1 gram P_2O_5.

(61) In complex analysis when the amount of the magnesium ammonium phosphate precipitate is large it is advisable to dissolve it from the paper into a small beaker with dilute hydrochloric acid before the washing is completed: the paper must be thoroughly washed with hot water, the washings being added to the liquid in the beaker. On cooling and making slightly alkaline with ammonia the precipitate is again thrown down: it is then filtered and treated as already described.

a. Determination of copper.

To a known amount of the mixture, in an Erlenmeyer flask, add about 300 c.c. of water and about 15 c.c. of dilute hydrochloric acid: heat and pass hydrogen sulphide gas through the solution till, on boiling and allowing the precipitate to settle, the supernatant liquid appears colourless. (Wash everything that adheres to the delivery-tube carefully into the flask also.) Allow to settle and decant through a filter; wash with hot water once or twice by decantation and finally transfer the precipitate to the filter and wash thoroughly.

Carefully label and put aside the filtrate and washings, which now contain ferrous sulphate and an excess of hydrogen sulphide; treat this as detailed under ***b.***

To obtain the copper in a convenient form for weighing, pierce the peak of the filter-paper with a glass rod and wash the precipitate, together with that which adheres to the glass rod, through into a beaker placed underneath. Wash also the filter-paper and funnel with a little hot dilute nitric acid to ensure complete transference of all copper compounds to the beaker. Warm the mixture and add as much concentrated nitric acid as is required to dissolve the copper sulphide completely and no more. *Excess of nitric acid must be avoided.* As solution progresses sulphur will separate and will appear black owing to the undecomposed copper sulphide which it encloses. Heating with nitric acid must be continued until every trace of black has disappeared and no insoluble matter remains but a little sulphur. This usually is in the form of a compact mass: it is removed mechanically from the solution, washed free of adhering solution and the washings added to the contents of the beaker.

The solution now contains copper nitrate and an excess of nitric acid. Add potassium hydroxide solution in slight excess and proceed as directed in ***81.*** Calculate the copper found to $CuSO_4 5H_2O$.

b. Determination of iron.

The filtrate from the copper sulphide precipitate is now boiled until all hydrogen sulphide is expelled; this point can be ascertained by testing from time to time with a strip of filter-paper moistened with a solution if a lead salt. When quite free from hydrogen sulphide, cool the solution under the tap *at once* and then titrate with $\frac{N}{10}$ permanganate as explained in ***35.*** Calculate to $FeSO_4 7H_2O$.

c. Determination of ($''SO_4$).

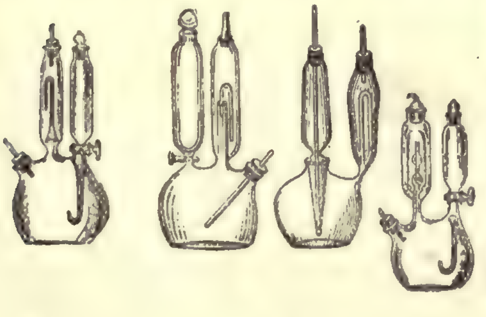
The copper and iron present in the mixture of sulphates having been determined, there only remains now the estimation of the $''SO_4$. To do this, take a fresh sample of the substance under examination, acidify slightly with dilute hydrochloric acid and proceed as laid down in ***82.***

88. Determination of carbon dioxide in a carbonate.

This can be done either by determining the loss in weight sustained by an apparatus containing the carbonate and the acid necessary to decompose it, after the action has taken place and the carbon dioxide has been expelled, or by directly weighing the carbon dioxide evolved when the carbonate is treated with dilute acid.

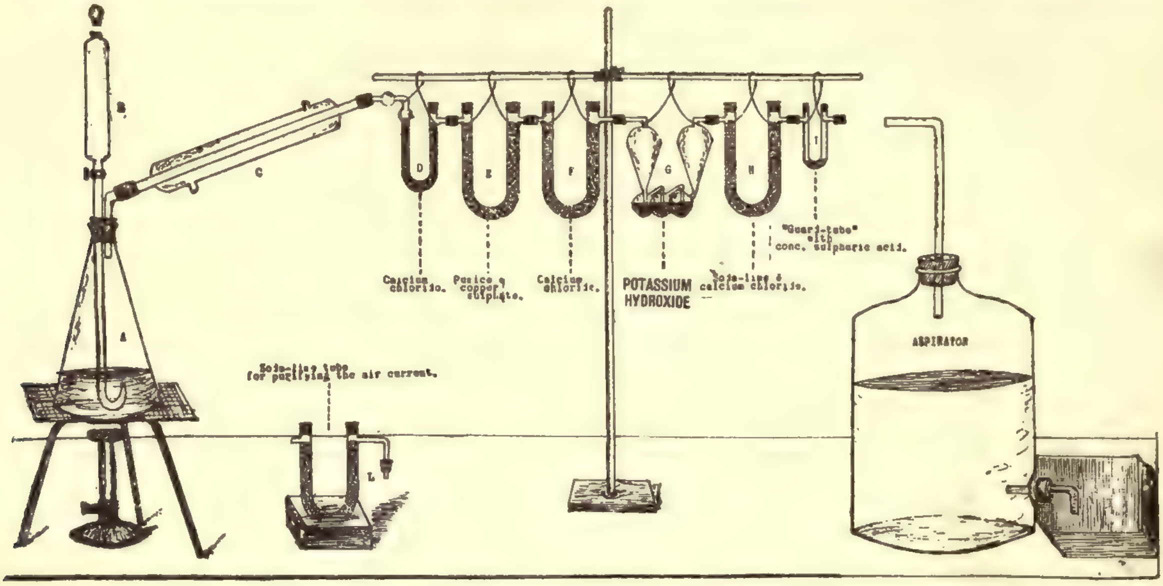
89. Determination by difference.

Numerous forms of apparatus have been devised for this purpose, a few of which are illustrated. The principle of each is the same: a known weight of the sample is placed in the bottom of the apparatus, dilute hydrochloric acid is put in the stoppered funnel and concentrated sulphuric acid half fills the exit-tube to dry the escaping carbon dioxide. The whole apparatus, with its contents, is weighed, the acid allowed to run in slowly and, when effervescence has ceased, heat is applied till all carbon dioxide has been driven out through the sulphuric acid trap. Carbon dioxide-free air is then sucked or forced through till the carbon dioxide is completely removed, when the apparatus is cooled and weighed. The gas must not escape too quickly or it will carry water vapour with it: only 2 or 3 bubbles per second should pass out through the sulphuric acid.



90. Determination by direct weighing.

The carbon dioxide evolved on treating the carbonate with dilute acid is absorbed by potassium (or sodium) hydrate, or by soda-lime, and weighed. The ideal acid to employ is sulphuric acid, being non-volatile, but in many cases the resulting sulphates of the metals present would be insoluble in water and would thus protect the remaining carbonate from the further action of the acid. Under these circumstances hydrochloric acid must be employed, though it has the disadvantage of being volatile. If the sample is suspended in water and hydrochloric acid added, the carbon dioxide evolved will contain moisture and gaseous hydrochloric acid (and, if the carbonate contains any decomposable sulphide, hydrogen sulphide). Arrangements are therefore made for absorbing these before they can reach the weighed tube containing the potassium hydrate (or soda-lime), whose function is to absorb the carbon dioxide only. The apparatus employed is illustrated in the figure. The carbonate, of which a weighed quantity is placed in the flask *A*, is decomposed by slowly running in dilute hydrochloric acid from the dropping funnel *B*, the extremity of which, drawn to a less diameter and with its end turned upwards to prevent gas-bubbles entering, dips below the level of the liquid. The air in the flask and the carbon dioxide pass out through the short inclined condenser *C* which prevents part of the water vapour from going any further. Tube *D* (containing granulated calcium chloride) frees the gas from moisture and tube *E* (containing fragments of pumice-stone previously saturated with copper sulphate by boiling with a concentrated solution of that salt and afterwards heating to dehydrate the copper salt) removes any hydrochloric acid gas and hydrogen sulphide. *F* ensures complete purification of the gas before it reaches the bulbs *G*, filled, as shewn in the figure, with potassium hydroxide solution (equal parts of potassium hydroxide and of water is a suitable concentration) and in which the carbon dioxide is absorbed, the tube *H* retaining any that may escape absorption in the potash-bulbs. *H* is filled $\frac{5}{6}$ of its length with soda-lime and the remaining $\frac{1}{6}$ with granulated calcium chloride ; the latter takes up any moisture that may evaporate from the soda-lime, the temperature of which rises considerably during the absorption of carbon dioxide. *I* is a smaller tube containing sufficient concentrated sulphuric acid in the bend to just stop it up and serves two ends ; it indicates the rate at which the gas is passing through the apparatus and it prevents any moisture finding its way into the weighed tubes from the aspirator *K*. The tube *L* contains soda-lime and has a connection ready to insert into the mouth of the funnel *B* after the reaction between the carbonate and the acid has ceased, when air, free from carbon dioxide and moisture, is drawn through the system to drive all carbon dioxide contained in it into the absorption tubes *G* and *H*. *L* and *K* are not connected up until the second stage of the experiment.


B
C
A
D
E
F
G
H
I
L
Calcium chloride.
Pumice & copper sulphate.
Calcium chloride.
POTASSIUM HYDROXIDE
Soda-lime & calcium chloride.
"Guard-tube" with conc. sulphuric acid.
Soda-lime tube for purifying the air current.
ASPIRATOR

The various connections are explained by the figure. The **U** tubes are filled amost up to the level of the side tubes, a loose plug of glass-wool being inserted between the granular absorbent and the latter to prevent any solid matter entering them. On the ends of the side tubes are fitted short lengths of rubber tubing, each closed at the end by a small piece of glass-rod, to protect their contents from the atmosphere. When an experiment is commenced the glass stoppers are removed and the rubber serves to connect the tubes. All joints and corks should be lightly paraffined and the whole apparatus must be perfectly gas-tight before it is used. To test if this is so, insert the cork at the end of the air-purifying tube *L* into the neck of the dropping funnel *B*. Attach a long piece of glass tubing to the side tube of *I*, letting the other extremity of it stand in a beaker of water. Then apply gentle suction when the water from the beaker will rise in the tube ; close the tap of the funnel and leave it to stand. If the level of the water and the level of the solution in the potash-bulbs remain stationary for about 10 minutes the apparatus is air-tight. If not, the leak must be found and remedied.

Instead of absorbing the carbon dioxide in a solution of alkaline hydroxide, some workers prefer using soda-lime. In place, therefore, of the potash-bulbs *G*, a **U** tube, charged similarly to *H*, is inserted. This substance, being in the form of a granular powder, presents a large surface to the action of the carbon dioxide, and its conversion into carbonate is accompanied by a considerable amount of heat. So much so, indeed, that the guard-tube *H*, becomes a necessity, intercepting any moisture originally present in the weighed soda-lime tube that may be expelled owing the high temperature the latter attains. The soda-lime is carefully sifted before use in order to remove the dusty portion which might tend to retard the passage of the gas. The heating and subsequent cooling of these tubes also serve as a useful guide to the progress of the absorption.

To perform the estimation, weigh from 1 to 5 grams of the powdered sample into the flask *A* and add hot water sufficient to cover the turn-up end of *B* when inserted. Remove the end stopper from *I*, half fill *B* with dilute hydrochloric acid (conc. HCl 1 part, water 1 part) and allow it to run into the flask slowly. *The operation must be so performed that the carbon dioxide is evolved and passes through the purifying and absorbing system sufficiently slowly to ensure complete absorption of each constituent.* When all effervescence has ceased circulate cold water through the condenser, attach the air-purifying tube (or towers) *L* to the funnel *B*, allow the remainder of the acid in *B* to run into the flask, connect the aspirator *K* to *I* and draw a slow current of air through the whole apparatus. Cautiously heat the contents of the flask to incipient boiling and keep the air current steady. When a sufficient time has elapsed remove the source of heat and increase the air current, keeping it going for about 10 minutes.

Remove the absorption vessels *G* and *H* to the balance, taking care to close their ends with the rubber tubes and glass stoppers ; cool and weigh. The increase in weight is the carbon dioxide.

PART II.

THE ANALYSIS OF SIMPLE MINERALS AND MINERAL PRODUCTS.

LIMESTONE OR DOLOMITE.

Limestone is essentially calcium carbonate, but generally contains magnesium carbonate; the presence of any considerable quantity of the latter causes the rock to be classed as a dolomite. Other constituents of the rock which are almost always present and which must be determined, are iron, aluminium, silica and phosphorus. The silica is generally in combination with the bases in the form of silicates insoluble in hydrochloric acid, though free silica in the form of quartz may be present also. Differentiation of the combined and free silica is sometimes desirable as it gives valuable information regarding the origin of the deposit. Phosphorus, when present, will be in combination with the metallic elements as phosphate.

91. The ***general plan of the analysis*** is as follows.—By treatment with hydrochloric acid separate into a soluble and an insoluble portion.

92. In the soluble portion. (1) Determine *iron and aluminium* together by precipitation with ammonia: weigh as Al_2O_3 and Fe_2O_3, (***78***). If desired, the proportions of these combined oxides can be estimated, (***109-111***).

(2) In the filtrate from the iron and aluminium precipitate, determine the *calcium* by precipitation with ammonium oxalate, (***85***).

(3) In the filtrate from (2), determine *magnesium* by precipitation with sodium phosphate, (***84***).

(4) In the soluble portion of a fresh sample, determine *phosphorus*.

93. In the insoluble portion.(62) (1) Determine *total silica* by fusion with alkaline carbonates, treatment with hydrochloric acid and dehydration. Weigh as SiO_2, (***98***).

(2) In the filtrate from the silica, determine the same metals as in the soluble portion and by the same methods.

In another sample of the mineral, determine the *carbon dioxide*, (***88-90***).

94. Weigh out from 1 to 2 grams of sample (dried at 100°) into a small beaker. Cover with a watch-glass to prevent loss by effervescence and introduce through the lip, by means of a pipette, from 15 to 20 c.c. of dilute hydrochloric acid. After the first violence of the effervescence has subsided, warm gently on a water or sand bath to complete the solution, adding a little concentrated hydrochloric acid if necessary. Evaporate to dryness, and to the dry mass add 10 c.c. of dilute hydrochloric acid, and about 50 c.c. of water: filter through a small filter-paper, and wash well with hot water (about 100 c.c. of wash water, properly used, should be ample). The soluble portion contains the greater part of the iron, aluminium, calcium and magnesium. The residue on the filter consists of silica and insoluble silicates of the above metals.

Analysis of the Soluble Portion.

95. Determination of Iron and Aluminium. Heat the solution almost to boiling, (the addition of a few drops of concentrated nitric acid may be necessary to oxidise the iron present), then add ammonia slowly, in slight excess. Stir well and boil for about 3 minutes. Filter, and wash the precipitate with hot water. The ammonia precipitates the hydroxides of iron and aluminium, which bring down with them a small quantity of calcium and magnesium. To free the precipitate from the latter, dissolve it off the paper into a clean beaker with as small an amount as possible of hot dilute hydrochloric acid. Wash the paper well with hot water. Dilute this solution to about 150 c.c., and precipitate with ammonia as before. Filter, and wash with hot water. This filtrate should be combined with that from the first precipitation. Then treat the precipitate as in ***78*** or place the filter-paper with the combined hydroxides in a crucible while still moist, and heat cautiously at first but finally with the blow-pipe for about 5 minutes. Cool and weigh as Fe_2O_3 and Al_2O_3.(63)

96. Determination of Calcium. The combined filtrates from the precipitation of iron and aluminium should be boiled down till the volume does not exceed 300 c.c. To the almost boiling solution add 5 c.c. of ammonia and then a slight excess of a boiling solution of ammonium oxalate. Continue to boil until the precipitated calcium oxalate becomes granular, set aside for an hour, filter and wash a few times with hot water. Ignite the precipitate and filter-paper in a platinum crucible; cool, and redissolve the calcium oxide in dilute hydrochloric acid, making the solution up to about 100 c.c. Again precipitate the calcium as oxalate by the addition to the boiling solution of ammonia and ammonium oxalate in excess, and treat as in ***85***.

(62) This may be dried at 100° and weighed. It generally consists of separated silica, clay, sand and organic matter. Where it is desired to determine the organic matter in a limestone, a convenient approximate method is to filter, after dissolving the sample, through balanced filter-papers: wash with hot water, dry the papers at 100°, and weigh: incinerate the filter carrying the insoluble residue (including organic matter) and weigh again. The loss in weight gives directly the amount of organic matter. The usual fusion is then made on the inorganic matter.

(63) It is seldom necessary to determine what proportion of these combined oxides is Fe_2O_3 and what is Al_2O_3. When necessary, however, this may be done precisely as given under Clay (***109-111***).

97. Determination of Magnesium. The two filtrates from the calcium precipitation are allowed to cool thoroughly and, if strongly alkaline with ammonia, made *almost* neutral by adding hydrochloric acid: next add about 20 c.c. of sodium phosphate solution and stir well, then 15 to 20 c.c. of ammonia, making the solution strongly alkaline once more, and follow the instructions laid down in ***84***.

Analysis of the Insoluble Portion.

98. Determination of Silica. Ignite the filter-paper containing the insoluble residue in a platinum crucible. When the ignition is complete add from 1 to 2 grams of dry sodium carbonate or of "fusion mixture."(64) mixing the contents of the crucible thoroughly with a stout platinum wire. Ignite strongly till the whole has been in a state of clear, quiet fusion for about 10 minutes: cool the crucible and place it in a small well-covered casserole (or deep porcelain or platinum basin) with about 20 or 30 c.c. of water. Add cautiously, a little at a time, enough concentrated hydrochloric acid to dissolve the fused mass and still leave the solution acid. Remove the crucible and wash it. Evaporate the solution to complete dryness on the water-bath and add 5 c.c. of dilute hydrochloric acid and enough hot water to complete the solution of the salts. Filter out the silica and wash, first with hot water, then with dilute hydrochloric acid and again with hot water. The washing of the silica must be very thorough to remove all traces of iron. Evaporate the filtrate a second time, take up with acid and water as before, and again filter out the silica, using a smaller paper than for the first filtration. Wash as before and repeat the process a third time, passing the solution through the second filter-paper.(65) The two filters now contain all the silica and are placed directly into a platinum crucible and ignited, gently at first, then strongly with a burner, finally with the blow-pipe till the weight is constant. Even when obtained in this way silica is seldom quite pure, though it may appear perfectly white. As a check on the silica, after being weighed add to the crucible's contents two drops of concentrated sulphuric acid, then about 2 c.c. of pure hydrofluoric acid: evaporate cautiously to dryness, ignite and weigh. The loss of weight represents almost exactly the amount of silica driven off as silicon tetrafluoride (SiF_4). The residue may consist of the oxides of iron, aluminium, or titanium, or of calcium sulphate. If present in any quantity it should be dissolved in hot hydrochloric acid and added to the original filtrate from the silica. Titanium is seldom present in any considerable amount.

99. Analysis of filtrate from Silica. This filtrate contains the same constituents as were present in that portion of the limestone which was soluble in hydrochloric acid. These should be determined in the same manner as before, though sometimes the two solutions are mixed and the determinations made at the same time. The principal objections to this procedure are: (1) Washing the precipitates is made more difficult on account of the large amount of alkaline chlorides in solution; (2) It is sometimes useful to know what proportion of the constituents occur in the soluble, and what in the insoluble portions.

100. Determination of Phosphorus.(66) As practically all limestones contain traces of phosphates, all the phosphoric acid will be precipitated in the form of ferric phosphate along with the ferric and aluminium hydroxides in the portion soluble in hydrochloric acid, and, of course, also in the filtrates from the silica. When it is necessary to determine the phosphates a fresh sample of about 5 grams should be used. The precipitate produced by ammonia (***95***), after washing, is dissolved in nitric acid and the phosphorus separated from the iron and aluminium salts as ammonium phospho-molybdate in which precipitate it is subsequently determined.

Treat about 5 grams of the sample as described in ***94*** and add ammonia to the soluble portion to precipitate ferric and aluminium hydroxides and the ferric phosphate. Wash as much as possible of the precipitate directly into a flask of about 500 c.c. capacity, provided with a good rubber stopper. Dissolve what remains on the paper in warm dilute nitric acid and add the contents of the flask, with as much more nitric acid as may be necessary to complete the solution. Add ammonia cautiously, till the precipitate which forms at first will just, but only just, dissolve

(64) An equimolecular mixture of the normal carbonates of potassium and sodium, or of sodium carbonate and potassium bicarbonate. Sodium carbonate alone is considered by some workers to be preferable to this mixture, potassium salts being more prone to pass into precipitates than sodium salts. The higher fusion point of sodium carbonate may also render it more effective in bringing about complete decomposition. It is recommended that from 4 to 6 parts of flux should be used for 1 part of sample. Larger amounts introduce more impurity than smaller ones and longer washing of precipitates is required. (*Bull. No.* 305, *U.S. Geol. Survey*, 1907, p. 72.)

(65) For technical purposes it is not usually necessary to exercise such care in dehydrating the silica as is directed above. In such cases the following procedure will suffice. After fusing and dissolving in hydrochloric acid, evaporate to dryness in a porcelain vessel, bake in a hot air-bath for two hours, keeping the temperature between 105° and 115°. Take up with 5 c.c. dilute hydrochloric acid and about 100 c.c. water, boil and filter. The silica remains on the paper and both it and the filtrate are treated as described in the text.

(66) See ***123***.

when agitated: if this point is passed, a few drops of dilute nitric acid may be added, and then more ammonia if necessary. The solution should now have the dark brown colour of neutral (not the light yellow of acid) ferric solutions; it should be perfectly clear and should not exceed 70 c.c. in volume. Heat the solution till it is as many degrees *above* 60° as the laboratory temperature is *below* 27°. Add to it an equal volume of an acid solution of ammonium molybdate(67) which must be at the temperature of the laboratory. Stopper the flask firmly, wrap in a towel and shake vigorously for five minutes, then allow to settle for the same space of time. Filter quickly through a small fine-grained paper, and wash by decantation with an acid solution of ammonium sulphate(68) till 5 c.c. of the washings give no colouration with dilute hydrogen sulphide water. When this point is reached, discontinue the washing and place the flask, which will still contain most of the precipitate, beneath the funnel. Pour 12 c.c. of dilute ammonia over the filter, to dissolve the ammonium phospho-molybdate; run this into the flask, wash the paper carefully with 100 c.c. of water and, if necessary, add a little more ammonia till a clear solution is obtained. Transfer this solution to a beaker and make it faintly acid with dilute hydrochloric acid: then add a crystal of tartaric acid, make alkaline again with dilute ammonia and allow tot cool.

Next add Magnesia Mixture and complete the estimation as insructed in ***86***.(69)

101. Should Manganese be present it can be estimated as described under Haematite, ***132***.

102. Determination of Carbon Dioxide. This is done as described in ***88-90***.

CLAY.

Clays are formed by the disintegration of rocks containing silicates of aluminium and consist of a mixture of real clay with quartz-sand, containing varying amounts of compounds of iron, calcium, magnesium, and the alkalies.

103. The following are usually estimated, being the most important constituents, and the proportions of which determine the character of the rock,—SiO_2, Al_2O_3, FeO, Fe_2O_3, MgO, CaO, Na_2O, K_2O, combined water, and carbon dioxide.

104. In technical work it is customary to make a mechanical analysis by which the coarse and fine sand are separated from the clay.

105. The ***general plan of the analysis*** may be outlined thus:

(1) Determine the *silica* by fusion with mixed carbonates, ***106, 107***.

(2) In the filtrate from the silica, determine *iron and aluminium*, ***108***.

(3) In the mixed oxides of iron and aluminium, determine the *iron*, ***109-111***.

(4) In the filtrate from the iron and aluminium precipitate, determine the *calcium*, ***112***.

(5) In the filtrate from the calcium, determine the *magnesium*, ***112***.

(6) A fresh sample of the clay is decomposed by heating it with its own weight of pure ammonium chloride and eight times its weight of precipitated calcium carbonate. The water-soluble portion of the fusion contains the alkali metals and calcium in the form of chlorides. The calcium salt is removed by precipitation with ammonia and ammonium carbonate, the ammonium compounds expelled by heat and the mixed chlorides of potassium and sodium weighed. In the combined chlorides the *potassium* is precipitated and weighed as potassium chloroplatinate: the *sodium* is thus determined by difference, ***113, 114***.

(7) In a separate portion, determine the *combined water*, ***115***.

(8) In a separate portion, determine the *carbon dioxide*, ***116***.

(9) In a separate portion, determine the amount of *iron present in the ferrous condition.* This is done by decomposing the rock in a sealed tube, by means of sulphuric acid. The solution is subsequently washed from the tube and titrated with potassium permanganate, ***117***.

106. Fusion and solution. The clay should be finely ground until when rubbed with the fingers no gritty particles are felt: it is dried at from 100° to 110° to constant weight.

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(67) To prepare ammonium molybdate, dissolve 50 grams of molybdic oxide in 200 c.c. of dilute ammonia (Sp. Gr. .96). Filter the solution and add slowly, with constant stirring, to 500 c.c. of nitric acid (Sp. Gr. 1.2). Warm to 45° and add 0.5 c.c. of a 10% solution of sodium hydrogen phosphate to ensure the saturation of the reagent with the phospho-molybdate. Stand in a warm place over night. The solution keeps best in the dark, and should always be filtered immediately before use. This reagent is sometimes made up from ammonium molybdate instead of by the foregoing method. That salt, as commonly sold, is not of certain composition; its use for the purpose is therefore not advisable.

(68) This solution is made by adding to 500 c.c. of water, 27.5 c.c. of dilute ammonia (Sp. Gr. 0.96) and 24 c.c. of concentrated sulphuric acid.

(69) For another method of estimating phosphates see Haematite, ***124***.

Weigh one gram of clay into an agate mortar and grind it up till mixed thoroughly with five grams of fusion mixture (mixed carbonates; see note (64)). Brush the mixture into a large platinum crucible, rinsing out the mortar by rubbing in it an additional amount (not exceeding 1 gram) of fusion mixture. The operation must be carefully performed over a sheet of glazed paper, in order that no loss may take place. Fuse thoroughly, and when cool transfer the crucible and contents to a moderately deep porcelain basin or casserole of about 15 cm. diameter. With the aid of a fine jet of hot water from a wash-bottle, and repeated small additions of hydrochloric acid, remove the fused mass from the crucible, and completely decompose the carbonates by further addition of dilute hydrochloric acid. Remove the crucible and thoroughly wash it with hot water, rubbing it at the same time with a policeman to remove adherent silica. Evaporate the contents of the casserole on the water-bath, spreading the pasty substance over as large a surface as possible.

107. Determination of Silica. Heat the contents of the vessel in an air-bath for two hours, between 105° and 115°, stirring from time to time in order to granulate the mass. When cool, add 10 c.c. of dilute hydrochloric acid and enough hot water to completely dissolve the chlorides. Filter, and treat as described under Dolomite, ***98***.

108. Determination of Iron and Aluminium. Dissolve, in a little nitric acid, any residue that remains after driving off the silicon tetrafluoride and add it to the filtrate from the silica. Boil the solution, add about 15 c.c. of dilute hydrochloric acid, then cautiously add ammonia till the solution is alkaline. Allow the precipitate to settle,(70) decant the clear liquid and wash the precipitate with hot water by decantation,(71) then finally, with great care, on the paper. Redissolve in hot hydrochloric acid and repeat the precipitation and washing. (The filtrates and washings from the two precipitations are used for the determination of Calcium and Magnesium, ***112***). Dry the precipitate, separate it from the paper, ignite the latter in a platinum crucible, add the former, and re-ignite, using the flame of the blow-pipe.(72) Cool and weigh the mixture of Fe_2O_3 and Al_2O_3.

109. Determination of Iron. The total amount of iron in the combined ferric and aluminium oxides must now be determined, after which the amount of aluminium is found by difference. The ignited precipitate of Fe_2O_3 and Al_2O_3 is seldom readily soluble in hydrochloric acid, so the following method of solution must be adopted. Place in the crucible (which should be a large one), containing the ignited and weighed precipitate, 5 grams of potassium pyrosulphate (fused potassium hydrogen sulphate), and heat gently with the flame of a bunsen burner for about one hour. The temperature should be so regulated that the mass is just kept liquid, and a slight evolution of sulphur trioxide is noticed, but should be as low as is consistent with these conditions being maintained. A fair degree of watchfulness is necessary, or loss may be occasioned by sudden overheating, and the projection of its contents from the crucible. When the fusion is complete (the fused mass should be clear and free from floating matter), allow the crucible to cool, rotating it meanwhile in such a way as to make the mass solidify round the sides rather than as a solid cake at the bottom. Place the crucible in a beaker and add enough water and dilute sulphuric acid to completely dissolve its contents.(73) Warm the solution almost to boiling and pass hydrogen sulphide gas into it till no further precipitation of sulphur (or platinum sulphide) takes place.(74 Cover the beaker and allow it to stand for a few hours (this renders the platinum sulphide easier to filter out), then boil and again pass in hydrogen sulphide to completely reduce the iron. Filter, while hot, into a flask through which a stream of carbon dioxide is being passed, boil to expel all hydrogen sulphide (continuing meanwhile to pass in carbon dioxide), cool and then titrate the iron with potassium permanganate. The hydrogen sulphide used must be very carefully washed or traces of iron may be carried over from the generator.

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(70) When a clay is poor in iron, the above precipitate generally settles very slowly, and is difficult to wash. When time presses, this difficulty may be overcome by adding a measured volume of a standardised solution of ferric chloride before precipitation. Allowance can subsequently be made for the amount of iron introduced in this manner.

(71) The prolonged washing by decantation is tedious at best, but the labour involved can be materially reduced by the following procedure. Arrange a beaker containing the precipitate to be washed in a position slightly above the level of a large porcelain dish: clamp into position a syphon fitted at its lower end with a small rubber tube and pinch-cock. As the precipitate settles in the beaker, draw off the supernatant liquid with the syphon, and run it into the dish, always taking care not to remove so much liquid as to draw over a visible quantity of the precipitate. Add more hot water to the precipitate, and continue this treatment until it has been sufficiently washed by decantation. As washings accumulate in the porcelain dish they may be boiled down and the solution kept at reasonable bulk. Finally pass these washings through a small separate filter paper, and later, add the precipitate so collected to the main portion.

(72) In cases where a blow-pipe is employed, the flame should be directed at the side, not the bottom of the crucible; it should not be allowed to completely envelope the crucible or its interior may become filled with reducing gases.

(73) Traces of silica may remain undissolved, due to incomplete dehydration in the first instance: should this be the case, filter the precipitate as in the main portion of silica, adding the amount obtained to that of the latter.

(74) It must be borne in mind that even platinum vessels are to some extent attacked in the course of a fusion, and that this is particularly the case when an alkaline pyrosulphate is used as a flux.

110. Another method for the determination of iron in the precipitate is as follows:—Fuse as before with potassium pyrosulphate and dissolve the contents of the crucible in water containing a definite amount of dilute sulphuric acid. Pass the solution slowly through a Jones reductor,(75) and wash the reductor with 150 c.c. of water. Titrate the solution in the reductor flask with potassium permanganate. It is usually necessary to make a blank determination with the reductor, immediately before or after, using the same volumes of liquid, sulphuric acid and wash water.(76)

111. Yet another method is as follows:—Fuse the mixed oxides of iron and aluminium with potassium pyrosulphate, extract the fused mass with dilute sulphuric acid, filter if necessary and reduce the ferric iron to the ferrous condition by bubbling sulphur dioxide through the solution. (Should sulphur separate filtration is advisable.) Transfer the solution, which must smell strongly of sulphur dioxide, to a conical flask provided with a cork and delivery tube bent over at right-angles. Clamp the flask to a retort stand and boil off the excess of sulphur dioxide, inserting the end of the delivery tube (when all the sulphur dioxide is apparently expelled) under the surface of a dilute solution of potassium permanganate contained in a test-tube held in the hand. As soon as the permanganate is no longer decolourised by the issuing gas, the flask and contents are cooled under the water-tap and the iron titrated with potassium permanganate.

112. Determination of Calcium and Magnesium. These elements are determined in the filtrate from iron and aluminium as described in ***96*** and ***97***.

113. Determination of the Alkalies. For this the clay must be ground to an impalpable powder. Weigh 0.5 gram into an agate mortar, add to it the same amount of pure ammonium chloride and grind the two together till they are thoroughly mixed. Next weigh out 4 grams of pure calcium carbonate,(77) add the greater part of this to the contents of the mortar and grind these till the mixing is complete. Transfer the mixture, by means of a brush and a sheet of glazed paper, to a platinum crucible of from about 20 to 30 c.c. capacity;(78) rinse out the mortar with the remaining portion of calcium carbonate and place these rinsings in the crucible. Cover it closely and apply the flame of a bunsen burner with great care so that the lower third, but no more, of the crucible is kept at a dull red heat. To aid in regulating the temperature it is very convenient to fit the crucible into a hole cut in an asbestos board, so that the upper portion is protected from the direct heat of the flame: or it may be embedded in calcined magnesia contained in a larger crucible and the heat applied to the latter. When the smell of ammonia is no longer perceived to proceed from the contents of the crucible, the heat may be slightly increased and should be continued for an hour. The mass should by this time have completely sintered together, but should not have been allowed to fuse into a solid cake. Place the crucible with its contents in a porcelain vessel and extract it thoroughly with boiling water. Filter and wash, at first by decantation. Should the residue contain any large lumps which do not easily disintegrate, they may be carefully transferred to an agate mortar, broken up, and washed back with hot water. The alkali metals and calcium, in the form of chlorides, will be found in the clear solution. It is well to test the residue by dissolving it in hydrochloric acid. Should it not dissolve from the filter completely, it would indicate that the mineral had not been entirely decomposed by the fusion.

Boil the solution, now containing the chlorides of calcium and the alkali metals, in a porcelain vessel, add 10 c.c. of ammonia and a slight excess of a freshly prepared solution of ammonium carbonate. Filter the solution into a platinum dish. Dissolve the precipitate in a slight excess of

(75) The Jones Reductor consists of a glass tube, about 2 cm. wide and 35 cm. long, slightly flared out at the upper end and drawn into a narrow tube at the lower. The latter passes through a perforated rubber stopper which fits the mouth of an ordinary filtering flask. Near the narrow end is placed a light plug of glass-wool and the tube is about two-thirds filled with well washed shot zinc (25 to 30 mesh), as free as possible from iron.

To reduce a solution by means of this apparatus, attach the charged reductor to the filtering flask, acidify the solution with about 5 c.c. of concentrated sulphuric acid, pour it into the reductor tube till the latter is filled well above the level of the zinc, and apply gentle suction through the flask so that the solution passes in a slow stream into it. Continue adding the solution, and follow it with about 200 c.c. of slightly acid wash-water, regulating the addition of the solution and washing and the strength of the suction so that no air is allowed to pass down the reductor till the washing is completed. (This precaution is necessary in order to avoid the formation of hydrogen peroxide.) Before using the reductor, if it has been allowed to stand, it should be well washed by passing through it 100 to 200 c.c. of water containing a little sulphuric acid.

Should the zinc used contain any appreciable trace of iron, a blank determination must be made immediately before the real analysis. The same volume of liquid, of the same acidity as the solution to be analysed, is passed through and is titrated after passing in order to determine the amount of iron taken up and consequently the amount of permanganate used by the impurity in the zinc, even when no reducible substance has been passed through. It is an advantage to have the zinc amalgamated as this precaution then becomes less necessary, unless the reductor has been much used since last it was charged. To do this, wash it thoroughly with water and pour on to it a solution containing about 1 gram of mercurous nitrate dissolved in 500 c.c. of water and 2 or 3 c.c. of nitric acid. Stir the zinc well, pour off the solution, wash repeatedly with water, then with water slightly acidified with hydrochloric acid and finally with pure water.

(76) An objection may arise to this method for the following reason. Should any titanium be present in the clay it will be reduced and oxidised at the same time as the iron: if any error is to be encountered through the presence of titanium, it is usually preferable that it should be made to fall on the aluminium rather than on the iron determination. Apart from such objections this method of determing iron is excellent.

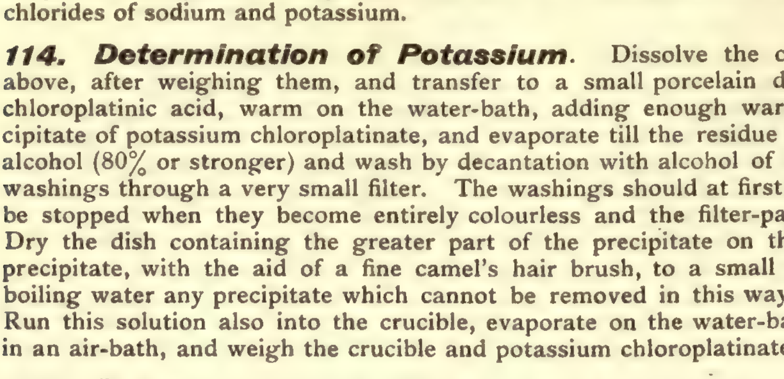
(77) The calcium carbonate and ammonium chloride should be specially prepared and used for this purpose only. Even when the greatest care is taken in their preparation they will not be entirely free from alkali and a blank determination should be made on each new sample.

(78) A thin layer of calcium carbonate placed in the bottom of the crucible before the mixture is added will prevent the fusion adhering to the crucible.

dilute hydrochloric acid and reprecipitate by ammonium carbonate. Add the second filtrate to the first and evaporate to dryness on the water-bath. Ignite the residue very cautiously over a small flame to drive off the excess of ammonium salts. A trace of calcium will almost certainly have escaped precipitation by the ammonium carbonate; it is removed in the following way: dissolve the residue from the expulsion of ammonium salts in about 10 c.c. of water, add two drops of ammonia and 1 c.c. of a solution of ammonium oxalate. Filter through a very small paper into a weighed platinum dish. Wash the paper thoroughly with hot water, evaporate the filtrate to dryness on the water-bath and again gently ignite. Add about 1 c.c. of concentrated hydrochloric acid, again evaporate and ignite. Weigh the dish with its contents, which will now consist of the combined chlorides of sodium and potassium.

114. Determination of Potassium. Dissolve the combined chlorides obtained as above, after weighing them, and transfer to a small porcelain dish. Add a decided excess of chloroplatinic acid, warm on the water-bath, adding enough warm water to redissolve the precipitate of potassium chloroplatinate, and evaporate till the residue becomes pasty. Add 30 c.c. of alcohol (80% or stronger) and wash by decantation with alcohol of the same strength, pouring the washings through a very small filter. The washings should at first be yellow, and the process may be stopped when they become entirely colourless and the filter-paper is free from yellow stains. Dry the dish containing the greater part of the precipitate on the water-bath, and transfer the precipitate, with the aid of a fine camel's hair brush, to a small weighed crucible. Dissolve in boiling water any precipitate which cannot be removed in this way and any adhering to the filter. Run this solution also into the crucible, evaporate on the water-bath, dry for half an hour at 130° in an air-bath, and weigh the crucible and potassium chloroplatinate (K_2PtCl_6).

115. Determination of Water. It will be evident at once that only when a rock is free from fluorine, chlorine, carbon, carbon dioxide, and oxidisable or reducible bodies can the water be determined by "loss on ignition." To obtain anything like accurate results the water driven off must be collected and weighed. This may be done in absorption tubes of various kinds but an ingenious and simple method is that of Penfield,(79) in which the rock is heated at one end of a narrow tube of hard glass as illustrated in the figure. The enlargements in the middle collect the water and prevent it running back and causing a fracture at the heated portion. Escape of steam during the ignition, due to air currents, can be prevented by fitting a short tube, drawn out to a capillary point, over the open end of the Penfield tube by means of a small piece of rubber tubing. Thoroughly dry the tube by heating it and aspirating dry air through it, then cool and weigh. Introduce a convenient quantity of the powdered rock into the bulb and weigh again, so obtaining the weight of the sample. Clamp the tube in a horizontal position and apply the heat of a bunsen burner to the mineral. The water will be driven off and will collect in the bulb, which may be cooled if necessary by applying wet filter-paper. When all has been driven over, fuse the tube behind the bulb in which the water has collected and draw the two portions apart. Allow the part containing the water to cool, then weigh it. Heat it again to drive off the water, aspirate the tube till quite dry and weigh again. In this manner the weight of the water is obtained directly. Care must be taken that the outside of the tube is quite clean. The powdered rock is best introduced into the bulb by means of a small thistle-tube, *d*, fine enough to fit into the interior of the Penfield tube and long enough to reach from end to end.



116. Determination of Carbon dioxide. When carbonates are present in a clay, carbon dioxide may be determined as described under **88-90**.

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(79) *Amer. Jour. Sc.*, XLVIII, 1894, p. 31.

117. Determination of Ferrous Iron. It frequently happens that, in an iron-bearing clay, a part of the iron is in the ferrous condition. The method for estimating iron already described results in the determination of the total amount present. To ascertain what amount of it is present in the ferrous condition, the following method of procedure should be adopted.(80)

Introduce about 0.5 gram of the very finely ground clay into a tube of resistant glass and draw out its open end somewhat to form a funnel through which acid may be poured. Add a very little water and boil briskly, so that the clay may be freely suspended in the liquid and may hold no air bubbles. Next add diluted sulphuric acid (about 2 parts concentrated acid to 3 parts of water by volume, and which has been previously boiled to free it from air) till the tube is three-fourths filled. Pass in a rapid stream of carbon dioxide (Fig. 1), delivered from a narrow tube made from the same glass as the decomposition tube, so that the subsequent sealing of them together may present no difficulty. While the stream of gas is still passing, heat the narrowest part of the decomposition tube and draw it out till the two tubes fuse together; then stop the stream of gas and rapidly seal off the delivery tube (Fig. 2). When the glass has cooled, place the sealed tube in an oven and heat at 170° or 200° till the clay does not appear to be further decomposed by longer heating. Allow the tube to cool, open it and rinse the contents into a beaker, dilute largely with water and titrate with a solution of potassium permanganate.

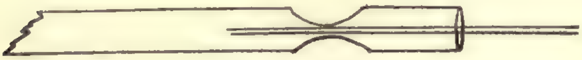

Fig. 1.

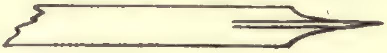

Fig. 2.

The foregoing method of displacing air from the tube before sealing is more difficult but much more effective than the one commonly employed, namely, dropping a few small crystals of sodium carbonate into the acid just before the tube is sealed.(81)

HAEMATITE.

Red haematite consists essentially of ferric oxide, while brown haematite is a partly hydrated ferric oxide: there is so little difference in the analytical methods to be employed that they may be considered together. The method of analysis adopted will depend on whether it is required for technical or scientific purposes; the former, being much shorter, will be considered first.

The constituents which it is generally necessary to determine are: iron, silica, sulphur and phosphorus.

118. The **general plan of the analysis** is as follows:

(1) Determine the *iron* by dissolving the ore in hydrochloric acid, reducing the ferric chloride and then titrating either with potassium permanganate in the presence of a "preventive solution," or with potassium bichromate. Should the residue insoluble in acid contain iron it is fused and the iron determined in a similar manner after being brought into solution.

(2) A separate portion is taken for the other determinations. It is dissolved as far as possible in hydrochloric acid containing a little nitric acid, the insoluble part being then fused, treated with hydrochloric acid and mixed with the rest of the solution.

(3) *Silica* is determined by evaporation and dehydration, and weighed by loss after treatment with sulphuric and hydrofluoric acids.

(4) *Phosphorus* is precipitated in the filtrate from the silica in the form of ferric phosphate along with the hydrated oxides of iron and aluminium, and is separated from these as ammonium phospho-molybdate, subsequently being determined by one of a variety of methods.

(5) *Sulphur* is determined in the filtrate from the precipitate produced by ammonia. It is precipitated by barium chloride (being present as sulphates) and weighed as $BaSO_4$.

119. Determination of Iron. The method here described is based on the following reactions: reducing ferric salts to ferrous salts by means of stannous chloride, removing the excess of the latter by precipitation with mercuric chloride, and titrating the ferrous salt with standard potassium bichromate or permanganate (**33**). Under ordinary conditions iron cannot be titrated with the latter in the presence of chlorides, but they do not interfere if present in only moderate amounts when a mixture containing manganese sulphate and phosphoric acid is previously added. Such a mixture is here known under the name of "preventive solution." This method gives good enough results for technical work if the standardisation of the permanganate and the subsequent titrations are done under exactly the same conditions.(82)

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(80) This method is not without defects. Errors may arise from (*a*) incomplete decomposition of the clay; (*b*) presence in it of sulphide (pyrites), its oxidation in the presence of the ferric salt and consequent reduction of the latter; (*c*) presence of carbonaceous matter. For a fuller criticism of this method see *Jour. Amer. Chem. Soc.*, XXII, 1900, p. 625.

(81) The following is the result of a (very incomplete) analysis of Chinese Kaolin:—SiO_2, 50.63%; H_2O, 10.01%; Al_2O_3, 32.74%; Fe_2O_3, 2.64% (total iron); CaO, .56%: MgO, .27%; K_2O and Na_2O, 2.52% (not differentiated).

120. Weigh out about 0.5 gram of finely ground ore into a small beaker, add 15 to 20 c.c. of dilute and 5 c.c. of concentrated hydrochloric acid: next add 2 c.c. of a solution of stannous chloride, made from 300 grams each of stannous chloride crystals and concentrated hydrochloric acid, heated till the solution is clear and added to a litre of water. Cover the beaker and boil. Should the liquid turn strongly yellow add (a drop at a time) more stannous chloride till the whole is once more colourless: the reaction is complete when the insoluble residue is quite white. Should the ore contain a ferruginous silicate this end cannot be attained: in such case filter the solution, wash moderately and set the filter and residue aside to be treated as described in **121**. A colourless residue need not be filtered out. If the solution, which should not exceed 30 c.c. in volume, is not slightly yellow, add a little potassium permanganate till a yellow colour appears (so avoiding the presence of an unknown excess of stannous chloride), then add stannous chloride, drop by drop, agitating the mixture after each addition, till the yellow colour is once more just discharged: next add, pouring rapidly, 10 c.c. of a saturated solution of mercuric chloride. The formation of a *white* precipitate of mercurous chloride will indicate that so far all has gone well, but should it turn after a minute or two to a dark precipitate of metallic mercury, it will show that the addition of stannous chloride was not made with sufficient care. In such case the only course is to repeat the analysis from the beginning. Next, quickly wash the contents of the small beaker into a large one and dilute to 500 c.c.; add from 8 to 10 c.c. of the "preventive solution"(83) and titrate quickly with a decinormal solution of potassium permanganate, (**33-38**), or of bichromate, (**43**).

121. Treatment of an insoluble ferruginous residue. In case that portion of the ore which does not dissolve in hydrochloric acid and stannous chloride is dark in colour, it should, as already stated, be filtered out. Place the paper, while still moist, in a platinum crucible, and ignite. Add about five times as much "fusion mixture" (*note* (84)) as there is silicate to be fused, and heat with a burner for 15 minutes. Cool quickly, place the crucible and contents in a small, well-covered beaker and add concentrated hydrochloric acid till all the carbonates are decomposed. Remove the crucible and wash it well. Boil the contents of the beaker and add a slight excess of ammonia; filter out the precipitate, wash with hot water, and dissolve from the paper with warm dilute hydrochloric acid. The solution so obtained may be added to the soluble portion before final reduction with stannous chloride, or may be independently reduced and titrated in the same manner. It is necessary to precipitate the iron as a hydrated oxide and to redissolve it, in order to avoid the presence of a large excess of alkaline chlorides, which would interfere in obtaining the proper end point of the titration.

122. Determination of Silica. Weigh out from 3 to 5 grams of ore into a small covered beaker, add 5 c.c. of water, 5 c.c. of concentrated nitric, and 15 c.c. of concentrated hydrochloric, acids; heat gradually to boiling, and continue to boil as long as any considerable amount of ore seems to dissolve; renew the hydrochloric acid from time to time if necessary. When the action is complete, dilute the solution with its own volume of water, filter, and wash thoroughly. Ignite the filter in a platinum crucible, and fuse the ash with five times its weight of sodium carbonate (or fusion mixture). Dissolve the mass from the crucible with hydrochloric acid, and unite this solution (including the floating particles of silica) with the filtrate first obtained. Evaporate to dryness, using a porcelain vessel, and taking care to spread the pasty substance over as large a surface as possible. Heat in an air-bath for two hours, between 105° and 115°, stirring from time to time with a glass rod in order to granulate the mass. When cool, add 10 c.c. of dilute hydrochloric acid, and enough water to dissolve all the chlorides. Boil for 5 minutes and filter out the silica; wash with hot water mainly, but from time to time pour a few c.c. of dilute hydrochloric acid over the filter, to avoid the formation of basic compounds. The filtrate contains the sulphur and phosphorus, and is used for their determination.

Place the precipitate in a weighed platinum crucible, without previous drying, and ignite, gently at first, then more strongly, and finally ignite with the blowpipe to constant weight. After weighing, treat with sulphuric and hydrofluoric acids and weigh again, as directed in **98**.

(82) *Analyst*, 1908, **33,** 43-47.

(83) Made as follows: 16 grams of manganese sulphate dissolved in 175 c.c. of water, and 33 c.c. of phosphoric acid (s.g., 1.7) and 32 c.c. concentrated sulphuric acid (s.g., 1.82), added.

123. Determination of Phosphorus. This determination is made in the filtrate from the silica. Boil the filtrate and add ammonia in slight excess, so precipitating aluminium hydroxide, ferric hydroxide, and ferric phosphate. Filter while still hot and wash very thoroughly with hot water, stirring the precipitate from time to time with a glass rod to ensure more complete washing. The sulphur will now be in the filtrate so obtained, and in this it is estimated; the phosphorus is contained in the precipitate as ferric phosphate and may be determined gravimetrically as described in **100**, or, more rapidly, by the following volumetric method.(84)

124. Treat the precipitate exactly as described in **100** up to the point where the ammonium phospho-molybdate(85) is obtained, redissolved in ammonia and the washings from the filter-paper added to this solution. Next shake the washings round the flask to completely dissolve the precipitate and add 80 c.c. of water and 10 c.c. of concentrated sulphuric acid. Pass through a Jones reductor,(86) washing the flask and reductor with 200 c.c. of water. Take care that in doing this no air is allowed to enter the reductor with the washings, or hydrogen peroxide will be formed and interfere with the titration. After the reduction, the solution will be dark brown to deep olive green. Immediately titrate with a decinormal solution of potassium permanganate without removing the solution from the flask of the reductor. During the titration the liquid becomes successively green, blue, colourless and pink. The latter is of course the end-point. A blank determination should be made on the reductor by running through it a mixture of 180 c.c. of water, 12 c.c. of ammonia (sp. gr. .96) and 10 c.c. of concentrated sulphuric acid, and immediately following with 200 c.c. of wash water.

This method depends on the fact that, when precipitated under the conditions laid down, ammonium phospho-molybdate contains 12 atoms of molybdenum to 1 atom of phosphorus; and further, that molybdic acid, in the presence of zinc and sulphuric acid, is reduced to derivatives of the oxide Mo_2O_3 which are readily oxidised by permanganate to those of MoO_3. 12 atoms of molybdenum thus correspond to 1 atom of phosphorus, and each atom of molybdenum requires 3 times as much oxygen for oxidation as is required for 1 atom of iron.(87) Each atom of phosphorus, therefore, will (indirectly) require $3 \times 12 = 36$ times as much oxygen as 1 atom of iron. So, if 1 c.c. of the standard permanganate is equivalent to x gram Fe, and 56 and 31 are the atomic weights of iron and phosphorus respectively, the phosphorus equivalent, y, of each c.c. of the permanganate will be found from the proportion,

$$36 \times 56 : 31 = x \text{ gram Fe} : y \text{ gram P},$$

i.e. $y \text{ gram P} = \dfrac{x \text{ gram Fe} \times 31}{36 \times 56} = .01548$ times the iron equivalent of the permanganate. In other words, to convert the iron equivalent of the potassium permanganate used for the titration into its phosphorus equivalent, multiply by 0.01548.

The method is very rapid and gives excellent results, but care must be taken to adhere rigidly to the conditions and on no account to interrupt the manipulation from the point at which the ammonium molybdate is added till the washing is complete. Failure to carry this part of the operation through continuously, or to observe the conditions of precipitation, may result in the deposition of molybdic acid with the ammonium phospho-molybdate; this would of course lead to a high result. The solution must also be titrated immediately after reduction and with as little exposure to air as possible.

125. Determination of Sulphur. This determination is made in the filtrate from the precipitate of hydrated ferric oxide and phosphate. Boil the filtrate down to a bulk not exceeding 300 c.c. Should ammonium chloride crystallise from the liquid, it may be destroyed by adding from 2 to 3 c.c. of concentrated nitric acid, and continuing the heating. Filter the solution, unless perfectly clear; then acidify slightly with hydrochloric acid, bring to a full boil, add 20 c.c. of a 10% solution of barium chloride, continue to boil for 15 minutes, allow to stand (well covered to guard from dust) till cold, filter through a small paper, wash with hot water till the washings are free from chlorides, transfer the moist filter to a weighed crucible, and ignite. To the cool contents of the crucible add two or three drops of dilute sulphuric acid (to reconvert any barium sulphide to sulphate), evaporate, ignite again, and weigh.

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(84) *Jour. Amer. Chem. Soc.*, 1895, XVII., 129.

(85) $(NH_4)_6 P_2O_5, 24MoO_3$. (?)

(86) See Note 75.

(87) Mo_2O_3 to become MoO_3 requires 3 atoms of oxygen, and 2FeO to become Fe_2O_3 requires 1 atom of oxygen.

126. For a more **complete analysis,** the following determinations will be also necessary: aluminium, manganese, calcium, magnesium; in brown haematite, water, barium, titanium and vanadium are not infrequently present in very small amounts, but for their determination larger works must be consulted.

It should further be remarked that, where scientific accuracy is desired, a slightly different method must be followed for the determination of silica; it is also advantageous to determine phosphorus gravimetrically instead of volumetrically.

127. The **general plan of a complete analysis** is therefore as follows:

(1) In a small separate portion determine *iron*, either by the method already given in **120, 121,** or by titration with standard potassium bichromate, **44**, **45**, **46**, and **119-121**.

(2) In a second and larger portion determine *silica*, *phosphorus* and *sulphur*. The silica is to be dehydrated in a somewhat different manner; the sulphur and phosphorus are separated as in the technical analysis, but the latter is finally weighed as magnesium pyrophosphate, **123**.

(3) In a third portion, remove the silica and then separate *iron* and *aluminium* (as the basic acetates) from the other metals present. Convert the basic acetates into hydroxides, and weigh together the oxides of iron and aluminium (with phosphorus as ferric phosphate). In the filtrate from the basic acetates, precipitate hydrated manganese dioxide by bromine, so separating it from calcium and magnesium. Convert the hydrated manganese dioxide to manganese ammonium phosphate, and weigh as *manganese* pyrophosphate. The filtrate from the hydrated manganese dioxide contains *calcium* and *magnesium*, which are determined as in Limestone, **96** and **97**.

(4) In a fourth portion determine the *water*, **134**.

128. Determination of Silica. The ore is brought into solution by the action of acids and by fusion, exactly as directed for the technical analysis, **122**. Evaporate the solution of chlorides to dryness, in a platinum or porcelain vessel, on the water-bath. Add 10 c.c. of dilute hydrochloric acid and enough water to dissolve the chlorides; boil for five minutes, filter, and wash the silica alternately with hot water and cold dilute hydrochloric acid. Evaporate the filtrate and washings a second time to complete dryness, take up with hydrochloric acid and water as before, filter through a small paper (not the same one used for the first filtration) and wash this second fraction of the silica. Again evaporate the filtrate, and again filter (using the second filter paper). Wash very thoroughly as before. The separation of silica is much more complete by this method and it is obtained in a purer condition than when dehydration is attempted at 115°. Burn the filter papers together in a platinum crucible, ignite gently at first, but finally use the blowpipe for 20 or 30 minutes. Weigh the crucible and contents, then add 2 drops of concentrated sulphuric acid and about 2 c.c. of hydrofluoric acid. Evaporate very cautiously and when dry ignite and weigh again. The loss of weight will give the amount of silica originally present, which has by this means been driven off as silicon tetra-fluoride. Dissolve the residue in the crucible by boiling with nitric acid, and add this solution to the filtrate. See also **98**.

129. Determination of Phosphorus. This determination may be made by either of the methods given for the technical analysis of the ore, but it is generally preferable, when rapidity of work is not essential, to use the gravimetric method. In the filtrate from the silica, precipitate and wash the ammonium phosphomolybdate exactly as described for the technical method. The filtrate and washings, however, should be further tested by being heated on a water-bath for 20 minutes with 100 c.c. of the solution of ammonium molybdate and adding any precipitate that may form to the first portion. The precipitate is then treated as described in **100**.

130. Determination of Sulphur. The same method should be used as in the technical analysis.

131. Determination of Aluminium. Weigh out a sample of 2 or 3 grams; bring it into solution and treat it exactly as in the determination of silica. The latter should, after being washed, be ignited and then driven off as silicon tetrafluoride, a check being so obtained on the first determination. Any residue from the driven-off silica should be dissolved in a little hot nitric acid and added to the filtrate.

To this filtrate add a solution of sodium carbonate, till the precipitate which forms as each drop of the alkaline solution falls into the solution of chlorides just redissolves on stirring vigorously. Should the proper point be passed, and a *permanent* precipitate be formed, reverse the process, adding dilute hydrochloric acid till the precipitate once more is just dissolved. The solution is now neutral, and should be clear and deep brown (not yellow) in colour. Next add 5 grams of solid ammonium acetate for every gram of iron present; if this operation has so far been properly carried out, the solution will be still clear, but deeper and redder in colour. Dilute the solution with water to 800 or 1000 c.c., and heat to boiling (it is at this stage that the precipitate appears); allow to boil for from 1 to 2 minutes only, then filter through a large ribbed paper *Keep the solution hot till the moment it is poured upon the filter.* Wash with boiling water twice The precipitate consists of the basic acetates of iron and aluminium, with ferric phosphate and adherent manganese, calcium and magnesium salts. To free it from the three latter metals, dissolve it in warm dilute hydrochloric acid, neutralise the solution and reprecipitate the basic acetates by the addition of ammonium acetate, dilution and boiling exactly as before. The whole of the manganese, calcium and magnesium will now be in the two filtrates, which should be combined. Owing to the large amount of adhering sodium salts, the basic acetates cannot be ignited directly to oxides. Redissolve the precipitate in warm dilute hydrochloric acid, add a slight excess of ammonia, boil for a few minutes, filter, and wash with hot water. The precipitate consists of ferric hydroxide, aluminium hydroxide, and ferric phosphate. Dry the precipitate, separate it from the paper and place in a small watch glass; place the paper in a weighed crucible and ignite gently. Cool and add the precipitate, again ignite, using the blowpipe till a constant weight is obtained. The iron and phosphorus having already been determined and calculated respectively to Fe_2O_3 and P_2O_5, the weight of Al_2O_3 is obtained by difference, since, for purposes of calculation, $FePO_4$ may be considered as $Fe_2O_3P_2O_5$.

132. Determination of Manganese. Combine the two filtrates from the basic acetate separation and concentrate them to about 500 c.c. Add 10 c.c. of 50% acetic acid and 5 c.c. of bromine and warm on the water-bath (under a good hood). Manganese is precipitated in the form of a hydrated dioxide. When all excess of bromine is expelled, filter the hot liquid, leaving as much precipitate as possible in the beaker, and wash with hot water. Calcium and magnesium are now in the filtrate, but the manganese cannot be advantageously ignited in its present form. Dissolve the precipitate from the beaker and the paper with dilute hydrochloric acid to which a few c.c. of sulphurous acid have been added; wash the solution into a porcelain casserole, make slightly alkaline with ammonia and add sodium hydrogen phosphate solution in slight excess: next add hydrochloric acid till the precipitate redissolves, warm the solution and add once more ammonia in *very* slight excess. Stir the solution and boil for a minute, then place it on the water-bath, and allow it to digest till the amorphous precipitate, which was at first formed, has become wholly crystalline. Filter, and wash with water. The precipitate is manganese ammonium phosphate (NH_4MnPO_4, H_2O). Dry the filter, separate the precipitate and filter-paper: burn the latter in a *porcelain* crucible, add the precipitate to it and ignite strongly. Weigh as manganese pyrophosphate ($Mn_2P_2O_7$).

133. Determination of Calcium and Magnesium. These metals are found in the filtrate from the hydrated manganese dioxide, and are separated and determined by exactly the same method as is indicated under the analysis of Limestone, **96** and **97**.

134. Determination of Water. This should be done as described in **115**.

The subjoined analyses may be of interest.

Locality.	Jackson Mine: Lake Superior.	Negunnee Manganiferous Haematite.
Fe_2O_3	93.75	65.40
MnO	trace	6.71
Al_2O_3	0.73	1.46
CaO	0.61	0.45
MgO	0.23	0.66
Sulphur	0.03	0.04
P_2O_5	0.32	0.16
Water and organic matter	1.09	2.46
SiO_2	3.27	22.67
	100.03	100.01

COAL.

135. The analysis of a coal for technical purposes generally includes the following determinations: *moisture*, "*volatile combustible matter*," "*fixed carbon*," *ash* and *sulphur*. The figures obtained in the determination of the first three of these must not be considered as representing any definite constituents of the coal; a variation in the method of analysis will almost always cause the results to vary somewhat, so that for the proper interpretation of those results it is necessary that the method be arbitrarily fixed and not diverged from. In spite of their indefiiniteness the results are of importance in judging the quality of a coal. Determinations of ash and sulphur are of course absolute and the results obtained by different methods on the same sample of coal no more vary than would the determinations of chlorine in a sample of common salt. The term "sulphur" is, however, intended to include only that portion present in the form of sulphides and not that which is almost always present as a sulphate. The amount of the latter has no technical significance.

136. Determination of Moisture. From 1 to 2 grams of the sample are weighed into an open (weighed) crucible or basin and dried for 1 hour in a hot air-bath, the temperature of which is kept between 104° and 107°. At the end of this time it is weighed again and the loss of weight considered as moisture.

137. Determination of Ash. The portion used for the moisture determination is here employed. Place the crucible (if such has been used) on its side and ignite, carefully at first, till all organic matter is burned out, stirring from time to time with a stout platinum wire to expose a fresh surface to the air and so help the combustion. When completely ignited the ash will be light gray or brown and must be constant in weight. The weight of this residue gives the amount of ash directly.

138. Determination of Volatile Combustible Matter. Weigh about 1 gram of coal into a platinum crucible of medium size (20 to 30 grams), cover closely, place on a triangle (which had best be of platinum also) and ignite, carefully avoiding draughts, for *exactly seven minutes* with the full flame of a bunsen burner. So adjust the crucible that its bottom is about 8 cm. above the top of the burner, the length of the flame being at least 20 cm. At the end of the seven minutes, by which time there should be no signs of combustible gases being evolved, cool the crucible and contents, wipe away any soot deposited on the *outside* of the crucible or lid and weigh. The loss of weight represents the volatile combustible matter plus the moisture plus half of the sulphur present as sulphides.

139. Determination of Fixed Carbon. This is found by difference. The weight of material left in the crucible after the determination of volatile combustible matter represents the fixed carbon plus the ash plus half the sulphur present as sulphides.

140. Determination of Sulphur. This is most usually made by some modification of Eschka's method: the following is convenient and works well.

Mix from 1 to 2 grams of finely powdered coal with 1 gram of magnesium oxide and 0.5 gram of anhydrous sodium carbonate. Place the mixture in a large platinum crucible, turn it on its side and heat gently, taking care not to fuse the contents, and stirring occasionally with a platinum wire. Continue the heating till the carbon of the coal is entirely oxidised. Allow the crucible to cool, transfer its contents to a beaker, add about 150 c.c. of water and boil for 5 or 10 minutes. Filter and wash the residue on the filter (it consists of unchanged magnesium oxide and the insoluble part of the ash) with hot water. To the filtrate add 15 c.c. of bromine water, boil for 5 minutes, acidify with hydrochloric acid, and continue the boiling till all bromine is expelled. Then add 10 c.c. of a boiling solution of barium chloride, continue the boiling for another 5 minutes, allow the barium sulphate to settle, filter and wash this precipitate with hot water till free from chlorides and treat it as described in **82**. Its weight is then calculated to sulphur.

In the above determination special care must be taken to use magnesium oxide as free as possible from sulphur. It is difficult to find a sample containing none, so a determination of the amount present should be made on a sample of about 20 grams and a suitable correction introduced in calculating the results of an analysis.

When particular exactitude is desired, the acidified solution should be evaporated to dryness and the small amount of silica dehydrated as described in **98**. The salts are then redissolved in water, the solution filtered and the analysis continued as before. An alcohol lamp should also be used instead of a bunsen burner during the combustion as coal gas is never quite free from sulphur compounds, the products of combustion of which may be absorbed by the alkali.

141. Calculation of results. The following results were obtained on a sample of bituminous coal.

Loss on drying at 105° – 107° for 1 hour (moisture)	0.970%
Loss on igniting for 7 minutes (moisture + volatile combustible matter + sulphur	29.330%
Ash	7.829%
Sulphur	1.416%

The amount of volatile combustible matter was therefore,

$$29.330 - (.970 + \frac{1.416}{2}) = 27.652.$$

The results of the analysis would be reported as follows:

Moisture	0.970 %
Volatile combustible matter	27.652 "
Ash	7.829 "
Sulphur	1.416 "
Fixed carbon (by difference)	62.133 "
	100.000 %

141a. While the composition of a coal conveys much useful information regarding its nature, there are other properties of which the numerical analytical results give little indication. In the case of bituminous or soft coals their ***coking qualities,*** the property possessed by them of forming caked masses of coke when subjected to destructive distillation, are of importance. The best coking coals give about 65% of coke, and such coals are consequently very valuable for metallurgical processes. In making the determination of the "volatile combustible matter" (***138***), the hardness and compactness—or the reverse—of the residue left in the crucible should be observed and noted.

Important also to the user is the ***Calorific Value*** of a fuel. To express such a factor numerically a standard unit of heat is required, and the one employed is the calorie. This is the amount of heat required to raise the temperature of 1 gram of water through 1°C. (best between the limits of 0° and 40° C).(87a) Employing this unit the "*Calorific Value" is the number of grams, kilograms, or pounds of water which* 1 *gram, kilogram or pound of the fuel can raise through* 1° *C*· Results of calorimetric determinations are often given in British Thermal Units, a B.T.U. being the number of pounds of water that can be raised through 1° Fah. by the combustion of 1 pound of the substance burned. The latter will evidently be $\frac{9}{5}$ of the former, as 1°C. is equivalent to $\frac{9}{5}$° on the Fahrenheit scale.

For example, if the heat evolved by the combustion of 1 gram of a coal were completely absorbed by 1000 grams of water, and, in the process, raised the temperature of the water through 8° C, then 8000 calories would have been evolved, and the "Calorific Value" of this coal would be stated to be 8000. That is to say, 8000 grams of water could be heated 1°C. by 1 gram of the coal; and, equally, 8000 *pounds* of water could be heated 1° by 1 *pound* of the coal. (This in B.T.Us. would be $\frac{9}{5} \times 8000$). Now it has been found that in order to convert 1 gram of water at 100°C. into vapour at 100°C, 537 calories are required: this number, 537, is known as the "latent heat of steam." Hence the "Evaporative Power" of the coal taken as an example would be $\frac{8000}{537} = 14.9$. (That is, the number of grams, kilograms, or pounds of water which 1 gram, kilogram, or pound of it could convert into vapour).

Numerous forms of calorimeters are employed for ascertaining the heat-producing qualities of a coal, but either defects and inaccuracies pertain to the use of the simpler forms or the difficulties in manipulating the high-pressure bomb instruments forbid their general use. A calorimeter which seems to combine simplicity with accuracy is that of S. W. Parr.(87b) It is based on the principle of causing the coal to undergo combustion in contact with sodium peroxide, which, besides supplying the oxygen required, is capable of absorbing the products of combustion, thus avoiding the liberation of these gases on the one hand or their retention under high pressure on the other. The following description of the apparatus is taken from the original paper.

(87a) The Kilogram-calorie, or large calorie, is the amount of heat required to raise the temperature of 1 kilo of water through 1°C.

(87b) *Jour. Amer. Chem. Soc.*, XXII., 1900, 646.

A (Fig. 1) is a copper vessel of a little over two liters' capacity insulated by two outer vessels of indurated fiber, B and C, so placed as to provide further insulation by the air space I. The cover is double to correspond with an air space between, the two parts being connected for convenience in handling. The cartridge D has an inside capacity of about 25 c.c. It rests on a pivot below and extends through the covers above and has a small removable pulley at the end. Turbine wings fastened to spring clips are placed on the cartridge, and a short cylinder E, open at both ends, is provided for directing the current set up by rotation of the vanes attached to the cartridge. The vanes are so set as to deflect the currents downward first along the cartridge and then up along the outside of the cylinder. The stem of the cartridge is so arranged as to permit the passage of a short piece of No. 12 copper wire (Fig. 2). It is, moreover, provided with a valve D at the lower end which prevents the escape of the enclosed air when heated by the combustion of the charge. The two ends B and C of the cartridge screw on. The process then is as follows: 1 gram of coal ground to pass through a 100-mesh sieve and dried in the oven as usual at 105°–110° is put into the cartridge, 16 to 18 grams of sodium peroxide are added, the top screwed on and the whole shaken to thoroughly mix the contents. The peroxide varies somewhat in fineness. It should practically all pass through a 25-mesh or 1 mm. sieve. After tapping the cartridge to settle the charge in the bottom, it is placed in the can and 2 litres of water added, the temperature of the water being 3° or 4° lower than the temperature of the work room. The pulley is connected by string to a small water or electrical motor giving about 50 to 100 revolutions per minute to the cartridge. When constant temperature is reached, the reading of the thermometer is taken and the hot wire is dropped through the valve into the charge, which is at once ignited and burns completely in two or three seconds. The extraction of the heat is effected in about five minutes and the reading of the maximum temperature is then taken. The number of calories due to the combustion of the coal is found from the formula

$$C = 0.73 \times w \times (t - 0.012^\circ)$$

where t is the rise in temperature of w the water employed.(87c)

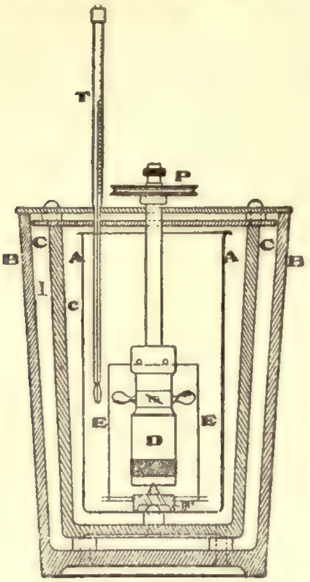
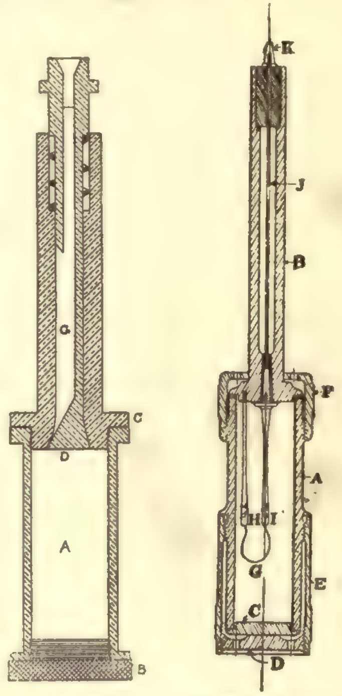


FIG. I. SECTION.



CARTRIDGE FOR WIRE IGNITION
FIG. 2.

CARTRIDGE FOR ELECTRIC IGNITION.

A practical example may be of value to the student:—beginning with water at 10° C, how many grams of a coal with a calorific value of 8000 would be required to evaporate 1000 grams of the water?

The amount of heat required to raise the temperature of 1000 grams of water from 10° to 100° C. is.. 90000 cal.

And the amount of heat required to convert 1000 grams of water at 100° C. into vapour at 100° C. is.. 537000 "

The total heat required is.. 627000 "

And 1 gram of the coal employed evolves 8000 calories:

Therefore the amount of coal required would be $\frac{627000}{8000}$ 78.37 grams.

(87c) This formula is obtained as follows. To the indicated rise in temperature t two important corrections must be applied: (*a*) the ho wire added to start the combustion has been found by Parr to give a rise in temperature of 0.012° C. per inch of the No. 12 copper wire employed t (*b*) the combination of the products of combustion with the sodium compound evolves an amount of heat found to equal 27% of the *total indicated heat*. So, letting C′ represent the total indicated, C the calories due to the combustion of the sample (1 gram), and w the weight of water employed in the calorimeter, then $C' = w\,(t - 0.012^\circ)$

$$\text{But } C = C' - \frac{27}{100}C'$$
$$= 0.73\,C'$$
$$\text{Therefore } C = 0.73 \times w \times (t - 0.012^\circ).$$

The number of *pounds* of this coal required to evaporate 1000 *pounds* of water, starting from 10° C, would be the same; for, in order to express in B.T.Us. the "heat required" and the "calories" which the coal is capable of evolving, the numbers found above must each be multiplied by the ratio $\frac{9}{5}$: this leaves the fraction $\frac{627000}{8000}$ unchanged. The number of *pounds* of the coal required for 1000 *pounds* of water is thus equal to the number of *grams* necessary to effect the same change in 1000 *grams* of water.

The problem might also be worked in B.T.Us. at once. To raise 1 pound of water through 180° Fah. requires 180 B.T.Us.

Therefore to raise 1 pound from 10° C. (*i.e.* 50° Fah.) to 212° Fah. requires 162 B.T.Us.

The "latent heat of steam" is $537 \times \frac{9}{5} = 966.6$ B.T.Us.

$\therefore$ the total heat required for 1 pound of the water = 1128.6 B.T.Us.
and $\therefore$ 1000 pounds require 1128600 B.T.Us.

But the coal has a calorific value of $8000 \times \frac{9}{5}$ B.T.Us.
$= 14400$ B.T.Us.

$$\therefore \text{ the amount of coal required would be } \frac{1128600}{14400} = 78.37 \text{ pounds.}$$

COPPER MATTE.

This substance, formed during the smelting of copper, is a mixture of the sulphides and oxides of copper and iron, but commonly contains also considerable amounts of lead, zinc, and arsenic.

142. For technical purposes it is seldom necessary to determine any constituent but the copper. The electrolytic method is almost universally adopted, and may be carried out as follows.

Dissolve about 0.5 gram of matte in 10 c.c. of dilute and 5 c.c. of concentrated nitric acid; a gentle heat will be sufficient to complete the solution. Evaporate to about half the original volume, then add 20 c.c. of water. Filter out the insoluble matter and wash thoroughly with hot water. Run the filtrate and washings into a weighed platinum dish: add ammonia till the solution is almost but not quite neutral and then add 2 c.c. of concentrated sulphuric acid. Electrolyse the solution, after diluting to a convenient bulk, making the dish the kathode. The conditions under which electrolysis is best carried out are, voltage 2-3, current 0.8-1 ampères for every 100 sq. cm. of cathode surface;(88) time, 0.2 gm. of copper will be deposited in about 1 hr. Complete precipitation may be insured by testing a few c.c. of liquid with hydrogen sulphide.(89) When it is seen that no more copper is present in the solution, syphon off the liquid, replacing it by hot water as rapidly as it is removed; next interrupt the current, pour off the water, wash the dish with a little alcohol, dry at 100° and weigh. Sometimes the solution to be electrolysed is placed in a beaker, the kathode being a suspended cone or cylinder of stout platinum foil. When this arrangement is used it is not necessary to filter the solution before electrolysis, since the insoluble matter settles to the bottom of the beaker and not on the kathode. The vessel in which the electrolysis is carried out should be covered by two slips of glass, fitting against the anode wire. The lower surface of these glasses will become covered with little droplets of the solution, carried up mechanically by bubbles of gas, and should be washed down from time to time.

143. For a **complete analysis** it is best to use two portions, one for the determination of the metals, the other for the determination of sulphur. For the former a convenient scheme is as follows.

(1) Dissolve in nitric acid as completely as possible, then evaporate with hydrochloric acid and filter out the *siliceous residue*, which will probably carry traces of lead sulphate: the latter is removed by washing with a solution of ammonium acetate and the recovered lead is added to the previous filtrate.

(2) In the filtrate from this residue, precipitate *copper*, *arsenic* and *lead* as sulphides. These should be reprecipitated to remove any trace of zinc which may have been carried down. They should then be separated as detailed in the sequel, being weighed separately as copper, magnesium pyro-arsenate and lead sulphate.

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(88) The current passing through an 8 c.p. lamp from a 110 volt circuit will nearly enough fulfil this condition should measuring instruments and rheostat not be at hand.

(89) Should this test shew that copper is still present, the tested liquid must of course be boiled with a few drops of dilute nitric acid and added again to the solution undergoing electrolysis.

(3) The filtrate should be oxidised, *iron* precipitated and reprecipitated as the basic acetate. It should be finally weighed as ferric oxide.

(4) In the filtrate from the iron, *zinc* may be precipitated as the sulphide and weighed as oxide, or as metallic zinc (after electrolysis).

(5) In another portion, *sulphur* is determined and weighed as barium sulphate. Any lead sulphate remaining in the insoluble residue is determined and calculated to sulphur.

144. The sample should not be too finely ground or it will be difficult to decompose. Dissolve about 0.5 gram of the copper matte in 10 c.c. of dilute and 5 c.c. of concentrated nitric acid. Apply heat only very cautiously at first. When the solution is almost complete add 10 c.c. of concentrated hydrochloric acid and evaporate to dryness. Take up with 5 c.c. of dilute hydrochloric acid and sufficient water to complete the solution. Filter out the insoluble matter and wash with hot water.

145. Determination of gangue. The insoluble matter consists of gangue with possible traces of lead sulphate. Pour over the filter 10 c.c. of a concentrated solution of ammonium acetate, then wash with warm water and add these washings to the filtrate previously obtained. Burn the moist filter paper and weigh the gangue in a porcelain crucible.

146. Separation of copper, lead and arsenic from iron and zinc. Dilute the above filtrate to about 500 c.c. Warm till nearly boiling, add 5 c.c. of dilute hydrochloric acid and pass in hydrogen sulphide till no more precipitate forms. Filter while still hot and wash with water saturated with hydrogen sulphide. Again test the filtrate with more hydrogen sulphide, to ensure the complete precipitation of arsenic. The precipitate is liable to carry down traces of zinc, but before freeing it from these it is best to separate the arsenious sulphide. For this purpose, digest the precipitate, on the paper, with 20 c.c. of a strong solution of sodium sulphide, then wash with water. Put aside the filtrates and washings, which contain arsenic as sodium thioarsenite, to be treated as described in **147**. Dissolve the mixed sulphides through the paper in hot dilute nitric acid; wash with hot water, dilute largely, warm and pass hydrogen sulphide till no further precipitate forms. Filter through the same paper and wash as before: the precipitate consists of lead and copper sulphides, **148** and **149,** and the united filtrates contain all the iron and zinc, **150, 151.**

147. Determination of Arsenic. This is present in the solution obtained by treating the mixed sulphides with sodium sulphide. To the solution add dilute hydrochloric acid, very cautiously, till the liquid is faintly acid. Filter out the precipitate of arsenic trisulphide and sulphur. Dissolve the arsenic trisulphide from the paper by treatment with about 20 c.c. of ammonia, and wash the paper with hot water. To the ammoniacal solution add an excess of nitric acid, then about 0.2 grams of potassium chlorate. Boil to complete the oxidation and expel all chlorine. Next neutralise with ammonia and add a slight excess of "magnesia mixture." Stir the solution well, and allow to stand for at least six hours. Filter through a *small* paper and wash the precipitate of magnesium ammonium arsenate with dilute ammonia. When the washing is complete, dissolve the precipitate from the paper by the use of a few drops of dilute nitric acid. Wash the paper thoroughly with hot water and allow the solution and washings to run into a weighed porcelain crucible. Evaporate to dryness and ignite. Weigh the arsenic as magnesium pyro-arsenate ($Mg_2As_2O_7$). (The precipitate is dissolved from the paper, and not burned directly, in order that there may be no chance of reduction, and consequent loss, of the arsenic).

148. Determination of Lead. Re-dissolve the mixed sulphides of lead and copper in hot dilute nitric acid. Place the solution in a porcelain vessel, add 10 to 15 c.c. of concentrated sulphuric acid, and evaporate on a sand-bath or hot-plate till heavy white fumes of sulphur-trioxide are evolved. Cool the acid liquid and add about 50 c.c. of water and 50 c.c. of 95% alcohol. Boil for a few minutes, then filter and wash with dilute alcohol till all the copper is removed. Dry the precipitate and treat it as directed in **83.**

149. Determination of Copper. The filtrate from the lead sulphate should be evaporated to expel all the alcohol. Partly neutralise the resulting solution by means of ammonia, and electrolyse, using the same conditions as to current, etc., that were given in **142.**

In cases where there are no facilities for determining copper electrolytically, it is best to re-precipitate it as the sulphide, then ignite the precipitate strongly in a porcelain crucible. Cool and add a few drops of nitric acid, evaporate cautiously and re-ignite (using a bunsen burner only). Weigh the copper as cupric oxide.

150. Determination of Iron. The filtrate from the sulphides of lead and copper contains iron and zinc. Boil this solution and add a few drops of nitric acid (or better, a few c.c. of bromine water) to completely re-oxidise the iron to the ferric condition. Filter out any sulphur that may separate, make the solution almost neutral and precipitate the iron as the basic acetate in the manner described in ***131***. The filtrate will contain the greater part of the zinc, but some will be retained by the basic ferric acetate. Dissolve the latter in hot dilute hydrochloric acid, boil the solution, and add a slight excess of ammonia: filter and wash with hot water. Dry the precipitate and separate it from the paper before igniting the latter. Finally ignite the whole and weigh as ferric oxide.

151. Determination of Zinc. This is contained in the two filtrates from the iron. Evaporate them together to a convenient bulk. Make the solution alkaline, and while warm pass in hydrogen sulphide (should any quantity of manganese, nickel or cobalt be present they will be readily detected by the discolouration of the white zinc sulphide, and suitable means may be taken for separating them. For such means larger works should be consulted) till the liquid is saturated. Allow the precipitate to subside. If no more forms in the supernatant fluid when more hydrogen sulphide is passed, the precipitation is complete. Filter and wash the precipitate with water containing a little ammonium sulphide and ammonium nitrate. Dissolve the zinc sulphide from the filter by means of warm dilute sulphuric acid. Collect the solution in a weighed platinum dish.(90) Add 1 gram of sodium acetate and 0.3 c.c. of acetic acid. Dilute to 150 c.c., warm to 65° C., and keep the liquid at this temperature while it is being electrolysed. Use a current of 0.36 ampère for 100 sq. cm. of cathode surface and an e.m.f. of 4 volts. At the end of about an hour the liquid will appear to be filled with bubbles. At this point, neutralise the liquid by adding a few drops of dilute ammonia, raise the current to about 0.7 ampère (5 volts) and continue the electrolysis. When a test shews that all the zinc has been removed, syphon off the solution, wash with alcohol, and finally with a little ether. Dry the deposit by holding the dish for a moment in the hand. Weigh as metallic zinc.

152. When it is known that no nickel is present in the filtrate from the iron (it is of very rare occurrence), precipitation of zinc sulphide may be entirely omitted, and the electrolysis proceeded with directly. About 0.1 gram of zinc is deposited per hour under these conditions, on a cathode surface of 100 sq. cm.

Zinc should never be electrolytically deposited directly upon platinum, as it leaves a spongy surface when redissolved. A platinum dish to be used for this purpose is readily prepared by depositing upon it a thin electrolytic coating of silver. A silver dish may be used as the kathode if it is conveniently at hand. When the electrolytic method is not available, the following course of procedure may be followed: precipitate and wash the zinc sulphide as already described and dissolve from the paper with dilute hydrochloric acid. Wash the solution into a porcelain casserole and add a slight excess of a recently prepared solution of sodium carbonate. Boil for 5 minutes, filter and wash with hot water till the precipitate is free from alkali. Dry the precipitate, separate it from the paper, ignite the latter in a porcelain crucible, add the precipitate to the ash and ignite strongly. Weigh the zinc oxide. This method, however, is not a desirable one.

153. Determination of Sulphur. Weigh out 0.5 gram of matte, add 20 c.c. of dilute nitric acid and heat very cautiously. After the first reaction has subsided add about 0.5 gram of potassium chlorate dissolved in cold concentrated nitric acid and continue to heat cautiously till all the sulphur has dissolved. Care must be taken not to raise the temperature too rapidly or part of the sulphur may fuse into globules which it will be almost impossible to oxidise. Evaporate with hydrochloric acid to expel nitric acid, then dilute the solution, filter out and wash the gangue. Preserve the latter for further examination, (***154***). Boil the filtrate, and add a slight excess of dilute ammonia; filter out the precipitate of ferric hydroxide, and wash with hot water. Boil the filtrate to expel the excess of ammonia. Acidify slightly with dilute hydrochloric acid, and while boiling add a slight excess of a solution of barium chloride. Allow the precipitate to settle, while standing in a warm place, filter and wash, by decantation at first, with hot water. Ignite precipitate and paper together in a weighed crucible; cool, add a few drops of dilute nitric acid and a drop of concentrated sulphuric acid (to convert any barium sulphide into sulphate), evaporate gently, ignite when dry, weigh the barium sulphate and calculate to sulphur.

(90) See *Jour. Amer. Chem. Soc.*, 1902, XXIV., 1073.

(91) A convenient alternative method of dissolving copper matte is to warm the powdered substance gently with 15 c.c. of concentrated nitric acid and 2 or 3 c.c. of bromine. The method applies equally well to the solution of natural sulphides (*See* ***156***). Its especial merit is that there is less danger of the sulphur forming insoluble beads.—*Jour. Amer Chem. Soc.*, XXII., 1900, 102.

154. The gangue may be contaminated with lead sulphate and the sulphur present in this form must also be determined. Digest it on the paper with about 10 c.c. of a strong solution of ammonium acetate (which will dissolve out any lead sulphate) and wash with hot water. To the filtrate add 5 c.c. of acetic acid and a slight excess of a solution of potassium chromate. Filter any lead chromate which may be precipitated through balanced filter papers. Wash with hot water, dry at 110°, weigh, and calculate the weight of sulphur to which it corresponds.

PYRITES.

The simplest member of this class of minerals is iron pyrites, FeS_2. Many metals, notably copper and nickel, may replace the iron, wholly or in part, while sulphur may be replaced by arsenic, and occasionally by antimony. Gold is also found in many samples of pyrites. For technical purposes it is usually sufficient to determine copper and nickel.

155. The ***general plan of analysis*** is as follows.—Both copper and nickel are determined electrolytically in the same portion of mineral. The former is deposited from a solution containing nitric and sulphuric acids. The latter is deposited from a solution of its sulphate, containing ammonia and ammonium sulphate.

156. Dissolve 1 gram of moderately ground pyrites, by pouring over it dilute nitric acid and gently heating on a water-bath.(92) After the reaction has proceeded for some time, add 10 c.c. of concentrated nitric acid, and raise the temperature, by bringing the water in the bath to the boil. Should the mineral not wholly dissolve, it may be boiled on a hot plate (or sand bath), concentrated nitric acid being added from time to time as required.

157. *Determination of Copper*. Cool the solution and add 10 c.c. of concentrated sulphuric acid; evaporate till all the nitric acid is expelled and heavy sulphurous fumes are evolved. Cool the solution, dilute to 50 c.c. by the cautious addition of water, and filter out the gangue—(if cylinder electrodes are to be employed later, the filtration may be omitted). Wash the filter paper well, and add to the filtrate enough ammonia to produce a *faint* precipitate of ferric hydroxide; add 1 c.c. of dilute sulphuric acid. Transfer the solution to a platinum dish, and electrolyse, observing the conditions laid down for the deposition of copper in **142**.

158. *Determination of Nickel*. The solution from which the copper has been deposited is used for this determination. Transfer it with the washings to a beaker, raise the temperature almost to boiling and precipitate the iron by adding a slight excess of ammonia, after ensuring the complete oxidation of the iron by adding a few c.c. of bromine water. Filter out the ferric hydroxide, which carries down with it some nickel. Wash it with hot water, then dissolve it from the filter paper by pouring over it warm dilute sulphuric acid. Re-precipitate the iron by means of ammonia and add this filtrate to the first. Again re-dissolve the iron and re-precipitate it, adding the filtrate to the first two.

Evaporate the filtrates, after adding a slight excess of sulphuric acid, till sulphurous fumes are evolved (this precaution is taken in order to drive off any nitric acid which may have escaped reduction during the deposition of the copper). Cool the solution, dilute to a convenient volume with water, add 5 grams of ammonium sulphate, neutralise with ammonia and add 30 c.c. of the latter in excess of what is required for that purpose. Transfer the solution to a weighed platinum dish, and electrolyse,(93) using an e.m.f. of about 3 volts, and a current of 0.5 to 1.5 ampères for each 100 sq. cm. of kathode surface.(94) The best deposit is generally obtained at the ordinary temperature, but quicker results follow by heating the liquid to 50°. Under the former condition, a current of 1.5 ampères deposits 1 gram of nickel in about 2 hours: at 50° the deposition is completed in nearly half the time. During electrolysis the dish must be covered by glass slips fitting against one another; these must be washed down from time to time. The reaction is complete when a drop of solution no longer gives a black precipitate when placed on a white surface in contact with a drop of ammonium sulphide. When this point is reached, syphon off the liquor, replacing it with hot water. Finally, interrupt the current, pour off the water, wash the deposit with a few c.c. of alcohol, dry at 100° and weigh. The deposit of nickel should be hard, bright and adherent.

(92) Solution may be also effected as described in **153.**

(93) Neumann—*Electrolytic Methods of Analysis*. English Edition (1898), p. 106.

(94) Where no measuring instruments are at hand, it is often convenient to pass the 110 volt "street-current" through a number of lamps arranged in parallel. The number and candle power of the lamps will serve to approximately regulate the current. The conditions above would be met by using two 16 candle power lamps in this way.

159. An excellent ***separation of iron and nickel*** may be effected as follows.(95) To the solution from which the copper has been electrolytically deposited add a few c.c. of bromine water, heat almost to boiling and add an excess of ammonia. Filter out the iron precipitate which carries with it some nickel. Dissolve the precipitate in hot dilute hydrochloric acid and evaporate till pasty. Add 10 c.c. of hydrochloric acid (sp. gr. 1.1) and transfer the solution to a separating funnel. Extract the ferric chloride by means of ether, as described in ***168***. The aqueous layer will contain all the nickel carried down by the ferric hydroxide. Add it to the filtrate from the latter, warm gently to expel the ether, then acidify with sulphuric acid and evaporate till sulphurous fumes are evolved: proceed with the determination of nickel as described in the previous paragraph.

160. A more ***complete analysis*** involves the determination of the following constituents: sulphur, arsenic, antimony, copper, lead, iron and nickel.

161. The ***plan of analysis*** is as follows:

(1) Dissolve a portion of the mineral and determine the sulphur (weighing it as barium sulphate) as described in ***153*** and ***154***.

(2) In a separate portion determine the other elements. Dissolve as before and, after filtering out gangue, precipitate arsenic, antimony, copper and lead by means of hydrogen sulphide. Arsenic and antimony should be separated from copper and lead by the use of a solution of sodium sulphide as described under the separation of arsenic alone from those metals in ***146***.

(3) Separate arsenic and antimony from one another by oxidising the solution of sodium thioarsenite and sodium thioantimonite by means of aqua regia. Precipitate arsenic as magnesium ammonium arsenate and, in the filtrate, determine antimony by the method described later.

(4) Separate nickel and iron by the repeated re-precipitation of the latter, as described under the technical analysis of this mineral (***158***). Determine the nickel electrolytically, as there described, and determine iron by weighing as ferric oxide. As an alternative, the iron and nickel may be separated by the ether extraction method (***168***) and the nickel determined as before. Iron may then be determined in a separate portion of the mineral, after separation from the nickel by three precipitations with ammonia, and weighed, after ignition, as ferric oxide.

162. The only point calling for more full description is the ***determination of arsenic and antimony.***

Dissolve the mineral as already described (***156***) in nitric acid, evaporate twice with concentrated hydrochloric acid, dissolve in water, filter out the gangue and pass hydrogen sulphide into the filtrate (which should be meanwhile heated) till precipitation is complete. Filter out the precipitate, which may consist of copper, lead, arsenic and antimony sulphides, and wash with water containing hydrogen sulphide. Arsenic and antimony sulphides will in this way pass into solution, while copper and lead sulphides remain unacted upon.

163. Separation of Arsenic and Antimony. Dilute the solution to 50 or 75 c.c. and acidify with dilute hydrochloric acid; add aqua regia, and warm gently at first, but more strongly later, till the re-precipitated sulphides are entirely dissolved. Filter out any sulphur which may remain unoxidised, and wash with hot water. Cool the filtrate and make it faintly alkaline with ammonia. Add 20 c.c. of "magnesia mixture" (*note* (60)), stir thoroughly and allow the whole to stand for 12 hours. Filter out the precipitate of magnesium ammonium arsenate and wash it with dilute ammonia; antimony will remain in the filtrate. Re-dissolve the precipitate of magnesium ammonium arsenate in a little hydrochloric acid (washing the paper thoroughly with of water), cool the filtrate, and re-precipitate by making strongly alkaline with ammonia. Allow 12 hours again for the re-precipitation and treat the precipitate as described in ***84***.

164. Determination of Antimony. Acidify the filtrate from magnesium ammonium arsenate with hydrochloric acid; almost boil the solution and at the same time pass into it a rapid stream of hydrogen sulphide. Filter the precipitate of antimony sulphide and wash it with a solution of hydrogen sulphide. Dissolve the precipitate by pouring over it about 25 c.c. of a *saturated* solution of sodium sulphide (made from the pure crystallised salt), and wash the filter paper with hot water. Catch the solution in a weighed platinum dish,(96) add a further 25 c.c. of a 20% solution of sodium sulphide and make up to a convenient volume with water. Warm the

(95) *Jour. Amer. Chem. Soc.*, XXII. (1900), p. 102.

(96) Neumann—*Electrolytic Methods of Analysis* (English Edition, 1898), p. 146.

solution to about 70° and maintain it at this temperature while it is electrolysed. The current for 100 sq. cm. kathode surface should be 1 to 1.5 amperes; e.m.f. 2 to 3 volts.(97) The dish must be closely covered to prevent loss by evaporation or spattering. When the electrolysis is complete, syphon off the solution, at the same time replacing it with a stream of distilled water. Interrupt the current, finally wash the deposit with alcohol and ether and dry by the heat of the hand. Weigh the dish with its adherent deposit of antimony.

165. When larger quantities of antimony are to be determined, a volumetric method may be used, such as the following :—

Dissolve the precipitated sulphide in a solution of sodium hydroxide. Add an excess of hydrochloric acid, 1 c.c. of nitric acid and successive small portions of potassium chlorate. Boil the solution down to 50 c.c. volume,(98) taking care that there is still some excess of hydrochloric acid present, in order that all the chlorate may be decomposed: cool the solution, add 15 c.c. of concentrated hydrochloric acid, and make up the solution to a volume of about 700 c.c.; add 3 or 4 grams of potassium iodide (free from iodate), and titrate immediately with a decinormal solution of sodium thiosulphate.

The reaction may be represented by the following equation: $Sb\,Cl_5 + 5KI = Sb\,I_3 + 5KCl + I_2$.

166. Another method of estimating the antimony is to re-precipitate in the filtrate from the magnesium ammonium arsenate precipitate (***163***) by adding hydrochloric acid and passing hydrogen sulphide. The precipitated sulphide is treated with nitric acid, dried, ignited and weighed as Sb_2O_4.(99)

NICKEL-STEEL.

167. Determination of Nickel in Nickel-Steel. The following method has been extensively used for the separation of nickel from iron.(100) It is also applicable where iron has to be separated from copper, manganese, uranium(101) and zinc.(102) It is, unfortunately, only applicable where the metals are present in the form of chlorides and depends on the solubility of ferric chloride in ether containing hydrochloric acid. Its superiority to any method whereby iron must be precipitated and re-precipitated is at once obvious. The separation is also very clean and complete. The exact manipulative details vary somewhat according to the metals present. For instance, it is necessary to make three extractions to completely separate iron from uranium.

168. The method of separation, which was referred to in ***159***, is as follows:

Weigh out 2 grams of nickel-steel into a porcelain dish or casserole provided with a good cover. Dissolve the steel in dilute hydrochloric acid, with the aid of heat. Add 1 c.c. of concentrated nitric acid, to oxidise ferrous to ferric chloride, and evaporate the solution to complete dryness. Dissolve the mass in 20 c.c. of dilute hydrochloric acid and evaporate again to a bulk of 10 c.c.; transfer to a separating funnel of about 250 c.c. capacity, washing the dish with the smallest possible quantity of dilute hydrochloric acid. Cool the solution thoroughly and add 40 c.c. of ether, which must be free from alcohol and must have been just previously shaken with 60 c.c. of dilute hydrochloric acid. Shake vigorously for 10 minutes, cooling the contents of the funnel from time to time. Separate the aqueous from the ethereal layer, washing the latter (which now contains all the iron) twice with from 5 to 10 c.c. of dilute hydrochloric acid. Gently warm the aqueous layer to expel ether and proceed with the determination of nickel by the usual methods, (***158***). Sometimes a second or third extraction with ether is necessary to completely separate all iron.

ANALYSIS OF IRON.

169. As commercially known, iron and steel contain, as accessory constituents, carbon, sulphur, phosphorus, and silicon, the accurate determination of all of which is very important for technical purposes. Other metals are also often present; most pig-iron contains a small quantity of manganese, (***181***); nickel-steel is commonly met with in commerce (***167, 168***), and steels are now being used which contain molybdenum, tungsten, uranium and other metals; titanium is also frequently contained in pig-irons. The methods employed in determining these constituents will not, however, be considered here; the determination of the non-metallic constituents only will be dealt with.

(97) *See Note* 94.

(98) The precise conditions of success with this method are given by L. A. Youtz, Inaug. Diss. Columbia University, 1902, with a critical study of the limits of its accuracy and applicability.

(99) *Jour. Soc. Chem. Ind.*, XXI., p. 748

(100) *Jour. Amer. Chem. Soc.*, 1899, XXI., 854. *Chem. News*, 1892, 66, 182.

(101) *Jour. Amer. Chem. Soc.*, 1901, XXIII., 689.

(102) *Jour. Amer. Chem. Soc.*, 1902, XXIV., 1211.

170. The **general plan of analysis** is as follows.—For rapid and accurate work a separate portion should be taken for the determination of each constituent.

(1) **Determination of Carbon.** The carbon in iron is present both in the free condition, "graphitic carbon," and in combination as the carbide of iron, "combined carbon": it is usually necessary to determine not only the total amount present, but to differentiate between the amounts present in each condition. If the iron be dissolved in acid the uncombined carbon (graphite) remains behind and *the combined carbon is evolved as hydrocarbons.* Solutions of copper salts, however, are capable of dissolving iron, yielding ferrous salts and metallic copper; no hydrocarbons are evolved, and *both combined carbon and graphite separate out.*

i. To determine the **Total Carbon,** the sample is dissolved in a suitable solution of a copper salt and the separated carbon converted into carbon dioxide, either by an oxidising solution or by combustion in a stream of oxygen, and weighed in this form.

ii. **Graphite,** which remains after the iron is treated with an acid, is determined in a similar manner.

iii. **Combined Carbon** is determined by difference.

(2) **Determination of Sulphur.** The metal is dissolved in bromine-water, the iron precipitated by ammonia, the whole made up to a fixed bulk, filtered, and the sulphur precipitated as barium sulphate in an aliquot portion. Any residue insoluble in bromine-water is fused with sodium carbonate, the fused mass dissolved in water, acidified, and the sulphur therein contained determined as before.

(3) **Determination of Phosphorus.** A separate portion of the metal is dissolved in nitric acid, the oxidation of the phosphorus completed by adding potassium permanganate, and any hydrated manganese dioxide dissolved by the addition of ferrous sulphate. The phosphorus is precipitated as ammonium phospho-molybdate which is filtered, washed and dissolved in ammonia. The solution is then acidified with sulphuric acid, passed through a Jones reductor, and the reduced solution titrated with potassium permanganate (**124**).

(4) **Determination of Silicon.** A separate portion is dissolved in nitric acid and evaporated with sulphuric acid till all water is expelled. The hydrated mass is boiled with dilute sulphuric acid to bring ferric salts into solution, filtered, and the precipitate ignited. The silica (contaminated with ferric oxide) is weighed, and again weighed after treatment with hydrofluoric and sulphuric acids (**98**). The loss in weight represents the silica present and should be calculated to *silicon.*

171. Determination of Total Carbon, using Chromic Acid for its oxidation. The apparatus employed for converting the carbon separated from the iron into carbon dioxide is similar to that shewn in **90,** but should have a short length of combustion tubing filled with granulated copper oxide (kept in place by coils of copper gauze) inserted between the short condenser C and the first drying tube D. This rests in a short combustion furnace or is heated to redness during the combustion process by several bunsen burners and serves to oxidise to carbon dioxide any hydrocarbons that may be evolved. The apparatus must be set up and tested for leaks as described in **90**.

Place from 1 to 5 grams of the sample (depending on the amount of carbon present) in the flask A (about 250 c.c. capacity) and, by means of the dropping funnel, run in 15 c.c. of a solution of copper sulphate (200 grams of the crystallised salt to 1 litre of water). Allow the solution to act on the iron for a few minutes and then introduce (through the funnel) 15 c.c. of a saturated solution of chromic acid, following it by 135 c.c. of a solution made up of 35 c.c. of the chromic acid solution, 190 c.c. of water, 750 c.c. of concentrated sulphuric acid and 340 c.c. of a solution of phosphoric acid of sp. gr. 1.4.(103) Gradually raise the temperature of the flask, but take care not to hurry the operation, allowing about twenty minutes for the solution to reach its boiling point. At the same time draw a *very slow* current of carbon dioxide-free air through the whole system and boil for about two hours. Aspirate a volume of air through the apparatus equal to about eight times the capacity of the flask A, disconnect the absorption tubes G and H and weigh them. The increase in weight is the carbon dioxide produced by the oxidation of the total carbon in the sample.

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(103) Olsen, from whose book these quantities are taken, recommends that this mixture should be heated to boiling before use.

Solution of the sample in the copper salt may also be effected in a beaker and the residue of carbon afterwards transferred, by the use of a *small* quantity of water, to the flask connected with the absorption apparatus, and oxidised with chromic acid as described.

172. Total Carbon by combustion in Oxygen. The iron is dissolved in a solution of copper-potassium chloride which dissolves it more rapidly than copper sulphate. The precipitated carbon is collected on an asbestos filter (*note* (105)), washed, transferred to a platinum boat and converted into carbon dioxide by burning it in a stream of oxygen. Other works should be consulted for a full description of this process.(104)

173. Determination of Graphite. A sample of from 1 to 3 grams of the iron is placed in a beaker, nitric acid of sp. gr. 1.2 added in the proportion of 15 c.c. of acid to each gram of iron taken, and, if necessary, the beaker immersed in a vessel of cold water to moderate the action of the acid. When the solution of the iron is complete, only the carbon which was present in the iron in the form of graphite will remain undissolved. Dilute the acid solution and filter this off on to an asbestos filter:(105) free it from iron salts and from silica by successively washing it with hot water, with a hot solution of potassium hydroxide (sp. gr. 1.1) to remove silica, with dilute hydrochloric acid, with hot water again, and finally with alcohol followed by ether. Dry the asbestos filter and residue, place them in the flask of the apparatus used in ***171*** and determine the carbon by oxidation with chromic acid as described in that paragraph. The carbon may also be determined by burning it in a stream of oxygen as indicated in ***172.***

174. Determination of Combined Carbon. This, as stated before, is found by taking the difference between the percentage of total carbon and the percentage of graphite.

175. Determination of Sulphur.(106) Place in a flask 8 c.c. of bromine,(107) and 200 c.c. of water. Add, a little at a time, 5 grams of iron, care being taken to cool the flask after each addition. The reaction is quickly over; when it is complete, boil the solution (in a good draught) to expel the excess of bromine, filter, and wash the residue with water, and finally with a *little* dilute hydrochloric acid. This residue contains part of the sulphur and must be set aside for further treatment. Place in a 500 c.c. graduated flask 130 to 150 c.c. of a 10% solution of ammonia: add to this the filtrate and washings obtained above and make up the volume to the mark. Mix the contents of the flask thoroughly, by pouring back and forth into a clean and dry beaker. Filter out the ferric hydroxide by pouring on to a *dry* filter paper and *do not wash the precipitate.* Take, by means of a pipette, 300 c.c. of the alkaline filtrate and evaporate this in a wide beaker to about 100 c.c. bulk. This evaporation serves the double purpose of concentrating the solution and at the same time expelling much of the free ammonia, so avoiding, later, the formation of undesirable ammonium chloride. (During this evaporation it will be necessary to avoid as far as possible any contamination of the alkaline liquid by sulphurous products of the combustion of coal gas.) To the concentrated solution add 1 drop of dilute hydrochloric acid and 10 c.c. of a 10 per cent. solution of barium chloride. Keep the solution hot till the precipitate settles quickly after stirring, then filter, wash with hot water, ignite and weigh as usual.

To determine the sulphur in the residue, proceed as follows: add to it about 0.5 gram of sodium carbonate, place in a platinum crucible, and burn the filter (using an alcohol lamp in order that no sulphur may be introduced, as would be the case were a gas-flame used). Fuse, and complete the oxidation of the carbon by adding one or two small crystals of potassium nitrate. Dissolve the fused mass in water, filter, slightly acidify with hydrochloric acid, boil the solution, add 5 c.c. of a solution of barium chloride, and treat the precipitated barium sulphate in the manner already described.

(104) Fresenius; *Quantitative Analysis*, Clowes and Coleman; Olsen's *Quantitative Analysis;* Phillips' *Engineering Chemistry.* The attention of the student is also drawn to the *Report of the Committee on Standard Methods for the Analysis of Iron:—Trans. American Foundrymen's Association, Philadelphia Convention*, May, 1907, and *Jour. Amer. Chem. Soc.*, XXIX., 1372-1376.

(105) Some pure asbestos is ignited at a red heat in a porcelain crucible for half an hour to free it from organic matter. To make a convenient filter a piece of glass tubing about three inches long and three quarters of an inch in diameter is drawn out at one end to form a funnel resembling in shape the lower half of the tap-funnel shown in ***90.*** A stout piece of platinum wire is closely coiled and placed resting on the shoulder of the tube with one end extending down the narrow part of the funnel; the coil retains the asbestos in position and the projecting wire serves to push out the filter and precipitate previous to the combustion. Asbestos is roughly ground up with a little water and poured into the funnel and, as the water drains away (assisted if need be by suction), a layer of asbestos is formed on the supporting platinum spiral. On the top of this is then poured a mixture of water and *finely* ground asbestos which last, after draining, leaves a compact layer of asbestos which makes an excellent filter capable of retaining the most finely divided precipitate.

(106) *Jour. Amer. Chem. Soc.*, 1901, XXIII., 675.

(107) The bromine may be freed from any probable contamination with sulphur by distillation over solid sodium carbonate.

In calculating the results of this analysis it must be carefully remembered that while the barium sulphate resulting from the treatment of the insoluble portion represents all of the sulphur present in it, that obtained from the soluble portion represents only $\frac{3}{5}$ of the sulphur which originally went into solution.(108)

176. Determination of Phosphorus.(109) Place 2 grams of the iron or steel in a half-litre flask, and dissolve by adding 50 c.c. of dilute nitric acid (sp. gr. 1.18). Warm the flask gently at first, but when all action appears to have ceased, boil vigorously for about one minute. If much graphitic carbon has separated (as would be the case with a pig-iron) it is often advantageous to filter the solution into a similar flask, using as little wash-water as possible. To complete the oxidation of the solution, add 10 c.c. of a solution of potassium permanganate (12.5 grams of salt per litre), and boil till the pink colour is discharged. Add a few crystals of ferrous sulphate (*free from phosphorus*) till all precipitated hydrated manganese is dissolved. Cool the solution to about 50° and nearly neutralise it by adding ammonia (sp. gr. 0.90), for which purposes 8 c.c. should suffice. The remainder of the determination is carried out as described in **124**. Care must be taken to observe the proper temperature and other conditions in order to obtain complete precipitation of the ammonium phosphomolybdate.

177. Determination of Silicon. Weigh 1 gram of sample, add 30 c.c. of nitric acid (sp. gr. 1.13); then 5 c.c. concentrated sulphuric acid. Evaporate on a hot-plate until all fumes are driven off. Take up with water and boil till all the ferrous sulphate is dissolved. Filter through an ashless filter, with or without a suction pump, using a cone. Wash once with hot water, once with hydrochloric acid, and then three or four times with hot water. Ignite, weigh, and evaporate with a few drops of sulphuric acid and 4 or 5 c.c. of hydrofluoric acid. Ignite slowly and weigh. Multiply the difference in weight by 0.4702, which will give the amount of silicon in the sample taken.(110)

TECHNICAL METHODS FOR EXAMINING PIG IRON, CAST IRON OR STEEL.(111)

178. Evolution method for the determination of sulphur. Weigh 5 grams of drillings into a 300 c.c. Erlenmeyer flask fitted with a cork and delivery tube, the latter bent at right-angles and passing into a tall beaker containing water and about 15 c.c. cadmium chloride solution, made by dissolving 20 grams of the salt in 500 c.c. of water and adding 500 c.c. of concentrated ammonia. Add *quickly* to the contents of the flask 80 c.c. of dilute hydrochloric acid (1 to 1) and cork immediately. Place on a hot-plate and when the evolution of gas slackens heat gradually to boiling until only steam is passing over: then disconnect, retaining the delivery tube for use as a stirring-rod. To the contents of the beaker add a little starch solution and sufficient hydrochloric acid to dissolve the yellow cadmium sulphide, at the same time running in an excess of $\frac{N}{50}$ iodine solution, (**48, 52**). Titrate the excess of iodine with $\frac{N}{50}$ thiosulphate of sodium and from the amount of hydrogen sulphide found calculate the percentage of sulphur in the sample, (**53**).(112)

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(108) The above method appears to be unexcelled for accuracy, and is at least reasonably rapid. In the writers' opinion comparison of it with any other methods only serves to bring out more strongly its merits. The only well-known methods which can claim greater rapidity belong to the class of "evolution" methods. These depend entirely on the liberation and determination of sulphur as hydrogen sulphide. It is, however, now well known that in many cases the sulphur in iron cannot be wholly liberated in this form. Evolution methods, therefore, can only be considered where rapidity is of greater importance to the chemist than accuracy. They are treated of in **178.**

(109) *Jour. Amer. Chem. Soc.*, 1895, XVII., 129.

(110) This description is taken verbatim from the *Report of the Committee on Standard Methods for the Analysis of Iron.—Trans. American Foundrymen's Association*, 1907, as printed in the *Jour. Amer. Chem. Soc.*, XXIX., 1907, 1373.

The number 0.4702 is the factor $\frac{Si}{SiO_2}$, namely $\frac{28.4}{60.4}$.

(111) For what follows under this head the authors are indebted to Mr. E. S. Jolliffe, M.A., formerly Chemist to the Canada Foundry Company, Toronto, It describes exactly the methods employed by him in the daily analysis of samples of iron for commercial purposes.

(112) Both the solutions being $\frac{N}{50}$, and as each c.c. of such an iodine solution is equivalent to $\frac{17}{50 \times 1000}$ *i.e.*, 0.00034 grams H_2S and consequently to 0.00032 grams S, the percentage of sulphur in the sample of 5 grams will be (c.c. Iodine – c.c. Thiosulphate) × 0.00032 × $\frac{100}{5}$.

179. If either of the following methods is used the exact strength of the iodine solution need not be known. The latter is employed now in most iron and steel laboratories.

(*a*) The sulphur content of a sample of iron is found gravimetrically as in ***175***. An evolution determination is then made as described in ***178*** and the value of the iodine solution in percentage of sulphur per c.c. for the weight of sample taken obtained directly.(113)

(*b*) "Standardised Iron Drillings" (obtainable from the Bureau of Standards, Washington, U.S.A.) may be used, and the iodine value in percentage of sulphur obtained directly.

180. Determination of Phosphorus. A solution of 0.5 gram of the iron (or 2 grams of steel) in 80 c.c. of nitric acid of sp. gr. 1.135 (1 conc. acid to 3 of water) is recommended, and the phosphorus precipitated as ammonium phosphomolybdate in the manner indicated in ***176***. The subsequent process differs entirely. It is, however, employed extensively in steel-works laboratories.

Having obtained the precipitate $(NH_4)_6P_2O_8$, $24MoO_3$, transfer it and the filter paper to the flask in which the precipitation was made, add about 50 c.c. of water and sufficient standard sodium hydroxide solution from a burette to dissolve the precipitate, shaking the flask until this end is accomplished. Add a few drops of phenolphthalein and titrate the excess of alkali with standard nitric acid of similar normality. The difference in the readings is the amount of sodium hydroxide required to react with the ammonium phospho-molybdate, the reaction being represented by the equation,

$$2\,[(NH_4)_3PO_4,\ 12MoO_3] + 46NaHO = 2\,(NH_4)_2HPO_4 + (NH_4)_2MoO_4 + 23Na_2MoO_4 + 22H_2O$$

$$\therefore\ 920 \text{ grams NaHO} = 1877 \text{ grams amm. phospho-molybdate,}$$
$$= 31 \text{ grams phosphorus.}$$

$$\therefore\ 1 \text{ gram NaHO} = \frac{31}{920} \text{ grams phosphorus.}$$

But as each c.c. of normal NaHO contains 0.04 gram NaHO, therefore 1 c.c. of normal NaHO is equivalent to $0.04 \times \frac{31}{920}$ gram phosphorus.

Fifth-normal sodium hydroxide and nitric acid are recommended. The alkali may be standardised by means of "Standard Iron Drillings" of known phosphorus content, thus getting its value in percentage of phosphorus per c.c. for the weight of the sample taken.

SPIEGEL-EISEN AND MANGANESE ORE.

181. The determination of Manganese only will be considered. An excellent gravimetric method for technical purposes depends on the tact that ferric hydroxide is precipitated from solutions of ferric salts on the addition of an excess of zinc oxide.

182. Method of Analysis (Gravimetric). To 2 grams of spiegel add 30 c.c. of dilute nitric acid and boil gently in a small covered beaker till the metal is entirely dissolved. (If an ore is being examined, it should be dissolved in hydrochloric instead of nitric acid). It is not necessary to filter out the graphite which separates during this process. Transfer the solution to a 500 c.c. graduated flask, and partly neutralise by adding a solution of sodium carbonate: next add a thin paste of zinc oxide suspended in water, till the iron is completely precipitated and a slight excess of zinc oxide is present. At this point the precipitate collects together and settles readliy. Add water till the flask is filled to the mark, agitate the solution and allow it to stand for a few minutes. Filter through a *dry* filter paper, rejecting the first 20 c.c. that run through. From the filtrate remove 200 c.c. on which to perform the determination. To this solution add 3 grams of sodium acetate (crystallised), 3 c.c. of 30% acetic acid, and 40 c.c. of bromine water. Heat almost to boiling, stirring occasionally and adding more bromine water if the precipitation of hydrated manganese dioxide is not complete. Filter, and wash with hot water, and treat the precipitate as described in ***132***.

This method is both convenient and accurate when it is not desired to determine the iron at the same time. When this is wanted, however, the solution of nitrates must be converted to chlorides, and the "basic acetate" method of separation employed, (***131***).

(113) The percentage of sulphur obtained by the evolution method is generally lower than that obtained by the gravimetric method, due probably, to all the sulphur not being evolved as hydrogen sulphide.

183. A convenient volumetric method for the determination of manganese is based on the foregoing separation of iron and manganese by the use of zinc oxide, and on the fact that manganese sulphate or nitrate reacts, in hot dilute neutral solution, with potassium permanganate, in a manner which may be expressed by the following equation:

$$3Mn\,(NO_3)_2 + 2KMnO_4 + 2H_2O = 2KNO_3 + 4HNO_3 + 5MnO_2$$

Taking 55 as the atomic weight of manganese, 316 grams of permangate are thus equivalent to 165 grams of manganese. As a solution of permanganate that is decinormal when used for the titration of iron contains 3.16 grams per litre (***33***), each c.c. of such a solution will be equivalent to $\frac{1.65}{1000}$ grams manganese, namely .00165 grams.(114)

Proceed as described above for the gravimetric determination, (***182***), up to the point where, the iron having been separated and the solution filtered, an aliquot part is to be taken for the determination. For this purpose it will be sufficient to take 100 c.c. of the filtrate. Place this in a porcelain casserole,(115) add 200 c.c. of water and boil. While still almost boiling, run in a decinormal solution of potassium permanganate, stirring very vigorously the whole time. If the permanganate is run in rapidly, a more accurate result is likely to be obtained, and it is generally best to make a rough determination on one portion of 100 c.c. to learn how much may be added with rapidity and safety. *The brown precipitate will only settle well if thoroughly stirred* (or rather beaten, as though beating an egg) while it is forming. The end-point is reached when the supernatant liquid is faintly pink.

This method is extremely rapid and convenient, though some practice is required in judging the end-point. It is not, however, so accurate as the gravimetric method, since there is always a certain amount of permanganate decomposed through the catalytic action of hydrated manganese dioxide upon it. Its inaccuracy is reduced to a minimum if the solution of potassium permanganate used is standardised on a spiegel, and composition of which is accurately known, instead of upon iron. Should the manganese be present as a chloride (through decomposing the manganese ore with hydrochloric acid, for instance), it must be evaporated with a slight excess of sulphuric acid till all hydrochloric acid has been expelled before this method can be applied.

TOURMALINE.

This complex mineral may be considered as a silico-borate of aluminium and magnesium. The determination of boron presents considerable difficulty, and will be alone considered here. The method employed depends on two important facts, (1) the ready formation and low boiling point of methylic borate—$B\,(OCH_3)_3$—and (2) the ease with which free boric acid may be titrated with a solution of sodium hydroxide, using phenolphthalein as an indicator, *when a large excess of glycerol is present.*

184. Determination of Boron (as Boric Acid). Fuse 0.5 to 1 gram of finely ground tourmaline in a platinum crucible with 5 or 6 times its weight of potassium and sodium carbonates. Avoid, if possible, the use of a blowpipe. Chill the fused mixture somewhat quickly, and when cold roll the crucible gently between the fingers. The greater part of the mass will now

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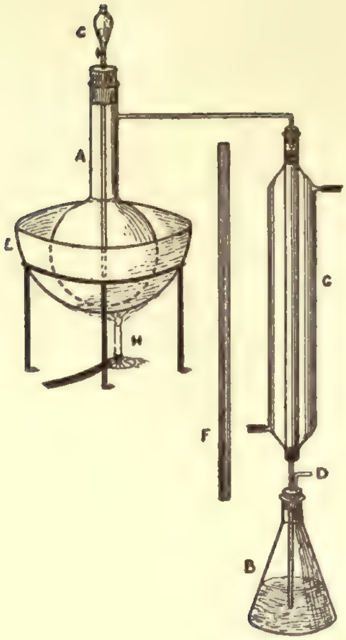
(114) The manganese equivalent of any solution of permanganate whose iron value is known can be obtained by multiplying this iron equivalent by 0.2946. This figure is found as follows: from the above equation it is seen that 3×55 grams manganese are oxidised by 316 grams permanganate, and from equation (a) in ***34*** it is evident that 10×56 grams iron are also oxidised by 316 grams permanganate. So, if 1 c.c. of the standard permanganate used is equivalent to x grams of iron, the manganese equivalent of that solution is found from the proportion $10 \times 56 : 3 \times 55 = x$ grams iron : y grams manganese.

$$i.e.,\ y \text{ grams manganese} = \frac{3 \times 55 \times x \text{ grams iron}}{10 \times 56} = 0.2946 \text{ times the iron equivalent.}$$

(115) Some workers prefer to make this titration in a conical flask with a tightly-fitting rubber stopper. In that case the flask is re-stoppered and vigorously shaken after each addition of permanganate. The effect in either case is the same.



drop from the crucible without difficulty. Having fitted up the apparatus shown in the figure, transfer the detached mass resulting from the fusion to the flask A which is placed in a bath of glycerine, E. F is a sheet of asbestos to protect the condenser G from the heat of E and of the burner. Rinse the crucible with sulphuric acid (1 part concentrated acid to 1 part water), add these rinsings to the contents of the flask, with as much more acid as may be necessary to strongly acidify the whole and to bring it to a pasty condition. Into the receiving flask B run 25 c.c. of deci-normal solution of sodium hydroxide. Let the condenser tube dip about 1 inch below the liquid. To the contents of the flask A add 10 c.c. of pure methyl alcohol, close the stopcock C, and raise the temperature of the glycerine bath till the distillate passes over freely. When the rate of distillation slackens, attach the tube D to a filter pump, and draw a slow current of air through the apparatus, regulating its speed by the stopcock C. Interrupt the air current, and add other 10 c.c. of methyl alcohol. Repeat this operation, alternately adding methyl alcohol and completely drawing it over (with the methylic borate formed) by a current of air, till 60 c.c. of methyl alcohol in all has been used. Then disconnect the flask B, run in 25 c.c. of deci-normal hydrochloric acid (thus exactly neutralising all the alkali present, and liberating all the boric acid), add 100 c.c. of glycerol and a few drops of phenolphthalein, and titrate with a deci-normal solution of sodium hydroxide, till a pink colour appears.(116 and 117)

The principal reactions involved may be expressed by the equations:—

$$Na_2O, B_2O_3 + H_2SO_4 + 2\,H_2O = Na_2SO_4 + 2\,B(OH)_3$$

$$B(OH)_3 + 3\,CH_3OH = B(OCH_3)_3 + 3\,H_2O$$

$$B(OCH_3)_3 + 3\,H_2O \text{ (in presence of alkalies) } = B(OH)_3 + 3\,CH_3OH$$

and for final titration,—$2\,B(OH)_3 + 2\,NaOH = 4\,H_2O + Na_2O, B_2O_3$.

(116) See also *Jour. Soc. Chem. Ind.*, XXV., 1906, p. 397: and *ibid*, XXVI., 1907, p. 803.

(117) The following analysis of a tourmaline from New Jersey is given by G. W. Sargent in the *Jour. Amer. Chem. Soc.*, XXI., p. 874:— SiO_2, 33.72; B_2O_3, 10.00; Al_2O_3, 25.88; Fe_2O_3, 1.82; FeO, 3.25; CaO, 6.92; MgO, 14.07; K_2O, 0.20; Na_2O, 2.52; Loss on ignition, 1.80 – per cent.

APPENDIX.

International Atomic Weights, 1911.

		O=16.
Aluminium	Al	27·1
Antimony	Sb	120·2
Argon	A	39·88
Arsenic	As	74·96
Barium	Ba	137·37
Bismuth	Bi	208·0
Boron	B	11·0
Bromine	Br	79·92
Cadmium	Cd	112·40
Cæsium	Cs	132·81
Calcium	Ca	40·09
Carbon	C	12·00
Cerium	Ce	140·25
Chlorine	Cl	35·46
Chromium	Cr	52·0
Cobalt	Co	58·97
Columbium	Cb	93·5
Copper	Cu	63·57
Dysprosium	Dy	162·5
Erbium	Er	167·4
Europium	Eu	152·0
Fluorine	F	19·0
Gadolinium	Gd	157·3
Gallium	Ga	69·9
Germanium	Ge	72·5
Glucinum	Gl	9·1
Gold	Au	197·2
Helium	He	3·99
Hydrogen	H	1·008
Indium	In	114·8
Iodine	I	126·92
Iridium	Ir	193·1
Iron	Fe	55·85
Krypton	Kr	82·9
Lanthanum	La	139·0
Lead	Pb	207·10
Lithium	Li	6·94
Lutecium	Lu	174·0
Magnesium	Mg	24·32
Manganese	Mn	54·93
Mercury	Hg	200·0
Molybdenum	Mo	96·0
Neodymium	Nd	144·3
Neon	Ne	20·2
Nickel	Ni	58·68
Nitrogen	N	14·01
Osmium	Os	190·9
Oxygen	O	16·00
Palladium	Pd	106·7
Phosphorus	P	31·0
Platinum	Pt	195·0
Potassium	K	39·10
Praseodymium	Pr	140·6
Radium	Ra	226·4
Rhodium	Rh	102·9
Rubidium	Rb	85·45
Ruthenium	Ru	101·7
Samarium	Sa	150·4
Scandium	Sc	44·1
Selenium	Se	79·2
Silicon	Si	28·3
Silver	Ag	107·88
Sodium	Na	23·00
Strontium	Sr	87·62
Sulphur	S	32·07
Tantalum	Ta	181·0
Tellurium	Te	127·5
Terbium	Tb	159·2
Thallium	Tl	204·0
Thorium	Th	232·0
Thulium	Tm	168·5
Tin	Sn	119·0
Titanium	Ti	48·1
Tungsten	W	184·0
Uranium	U	238·5
Vanadium	V	51·06
Xenon	Xe	130·2
Ytterbium (Neoytterbium)	Yb	172·0
Yttrium	Y	89·0
Zinc	Zn	65·37
Zirconium	Zr	90·6

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